Evaluating the Efficiency of Different Microfiltration and Ultrafiltration Membranes Used as Pre-treatment for Reverse Osmosis Desalination of Red Sea Water

Thesis by

Samer Khamees AlMashharawi

In Partial Fulfillment of the Requirements

For the Degree of

Master of Science in Environmental Science and Engineering

King Abdullah University of Science and Technology

Thuwal, Kingdom of Saudi Arabia

July 2011

EXAMINATION COMMITTEE APPROVALS FORM

The thesis of Samer Khamees Al-Mashharawi is approved by the examination committee.

Committee Chairperson Noreddine Ghaffour

Committee Member Jorg Drewes

Committee Member Tao Zhang

ABSTRACT

Evaluating the Efficiency of Different Microfiltration and Ultrafiltration Membranes Used as Pre-treatment for Reverse Osmosis Desalination of Red Sea Water

Samer Khamees Al-Mashharawi

With the increase in population density throughout the world and the growing water demand, innovative methods of providing safe drinking water are of a very high priority. In 2002, the United Nations stated in their millennium declaration that one of their priority goals was “To reduce by half, by the year 2015, the proportion of people who are unable to reach or to afford safe drinking water” [1]. This goal was set with high standards and requires a great deal of water treatment related research in the coming years.

Since 1990’s, drinking water treatment via membrane filtration has been widely accepted as a feasible alternative to conventional drinking water treatment. Nowadays, membrane processes are used for separation applications in many industrial applications. Over the past two decades, there has been a rapid growth in the use of low-pressure membrane for drinking water production. These membrane systems are increasingly being accepted as feasible and sustainable technologies for drinking water treatment.

Like any innovative process, it has limitations; the primary limitation is membrane fouling, a phenomenon of particles accumulation on the membrane surface and inside its pores. It has the ability to reduce the permeate flux so that higher pumping intensity is

required to maintain a consistent volume of product and increasing the cleaning frequency. This project has investigated the rate of reduction in the flux and the increase of pumping intensity using different membranes. Low pressure membranes with three different pore sizes (0.1µm MF, 100kDa UF, and 50kDa UF) have been tested.

Eight different filtration configurations have been applied to the membranes including the variation of coagulant ($FeCl_3$) addition aiming mitigation fouling impact in order to maintain consistent permeate flux, while monitoring several water quality parameters before and after treatment such as turbidity, SDI_{15}, total organic carbon (TOC) and particle size distribution.

Collectively, results showed that all eight configurations provided permeate with excellent water quality to be fed to reverse osmosis membrane. However, using the 0.1 µm and 100kDa membranes with 1 mg/l $FeCl_3$ concentration, respectively, steadier fluxes correspond to less increment of pumping intensity and better water quality was achieved.

ACKNOWLEDGEMENTS

The completion of this thesis would definitely not be possible without the help, support and motivation of several important individuals.

First and foremost, I would like to thank my supervisors and chair committee Dr. Noreddine Ghaffour for his exceptional expertise and advice along the way and my committee members Dr. Jorg Drewes and Dr. Tao Zhang for their guidance and support.

My appreciation also goes to the Water Desalination and Reuse Center lab manager Dr. Faisal Wali and the research technicians: Mrs. Sadaf Umer , Mrs. Tong Zhan and Mr. Ahmed Khasmi for their great help, guidance and support throughout my experimental work in the lab.

I would also like to thank all of my friends and colleagues in the department for all kind of help and support they provide and for making my research work to be such a great experience. I also want to extend my gratitude to the Coastal & Marine Resources Core Lab staff who provided the deep sea water needed to run the experiment, and to all the King Abdullah University of Science and Technology Professors and students who were willing to participate in the study.

Finally, my heartfelt gratitude is extended to my parents for their encouragement and support.

TABLE OF CONTENTS

LIST OF ILLUSTRATIONS

LIST OF TABLES

Chapter I

1.1 Introduction

In the late seventh century AD Jabir Ibn Hayyan had established the rules of distillation and classified them by his greatest invention called alembic [2]. Since that time this technique has been developed and used widely in different fields and among them is the production of distillate water. Desalination refers to the various processes designed to separate salt from water and produce treated water with different qualities depending on the end user requirements [3]. Nowadays, desalination is being widely used all over the world for different purposes e.g. producing fresh water for municipality and public use, for agriculture and irrigation uses, treated water for industrial uses, etc…. Even though producing desalinated water is expensive but in water-short regions in the world it is considered to be vital for economic development [4]. Particularly, desalination is an important and the main source for receiving drinkable and fresh water in the arid regions in the Middle East such as the Arabian Gulf Council Countries (GCC) and some countries in North Africa [5].

Desalination market is increasing sharply not only in the Middle East and North Africa (MENA) countries but all over the world [6] , since the reserves of natural fresh water are decreasing and the worldwide demand for fresh water in increasing [7]. Also, the cost of desalination is getting less as well as it guarantees the quality of the produced water compared with other traditional ways of getting potable water [5]. The International Desalination Association (IDA) reported that the total capacity of the plants that are completed by 2010 reaches 65.2 million m^3/d and additional 6.5million m^3/d are in commission for the near future [6]. Around 1895, the first seawater desalination plant was built in Jeddah, Saudi Arabia named Kindasa and it was a single effect distiller followed by a multi effect distiller in some other regions in the country such as Alkhobar and Dhahran [4]. In nineteen fifties the first multi stage flashing (MSF) was applied in Kuwait [4]. While in Europe the first desalination plant operated in 1928 in the Netherlands Antilles [5].

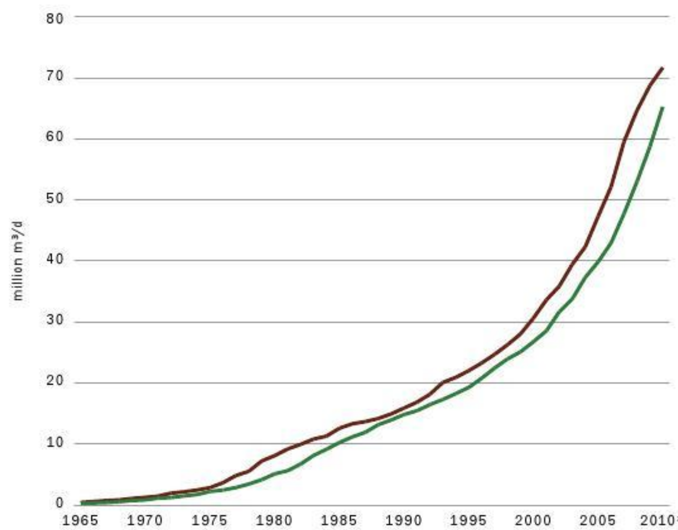

Figure I.1 shows the capacity of contracted (Red line) and commissioned (green line) desalination plants, 1965-2010 [6]

Nowadays almost 50% of the global desalination capacity is being produced in the MENA countries which is about 24 x 10^6 m^3/d. The figure below shows the most of those countries and their corresponding desalination capacities [4, 6]. This number is going to increase in the MENA and the world in general as the urbanization and growth are increasing. At present, 25% of Saudi oil and gas production is used locally to generate electricity and produce water and this fraction will be 50% by 2030 [8]. All these facts increase the importance of searching and implementing a less energy consuming and more sustainable desalination process.

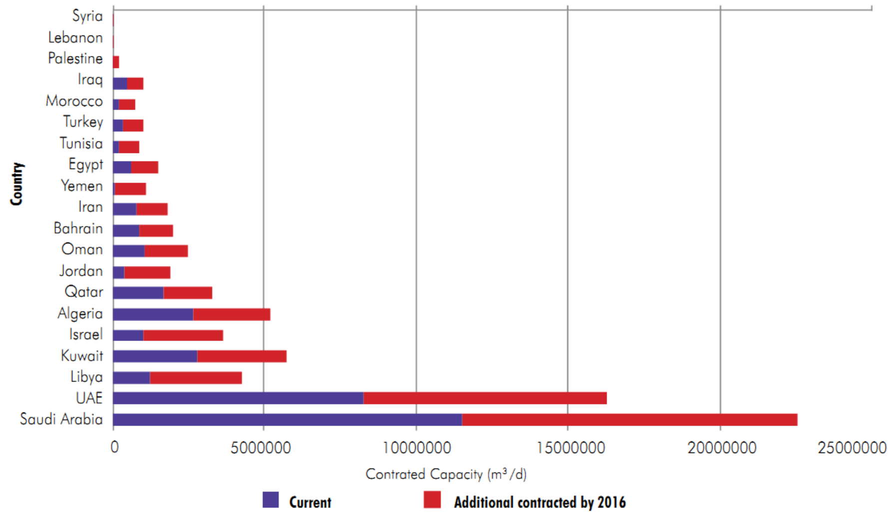

Figure I.2 Contracted and commissioned desalination plants in MENA, current-2016[4]

Different desalination technologies are being used globally depending on the feed water source, economic factors and others. All the previously mentioned in the history of desalination plants were based on thermal evaporation processes to mimic the natural hydrological cycle to desalinate seawater but it is high energy consuming process [9]. However, in 1970s a newer technology began to be used that is membrane technology that mimics that biological process of osmosis and it has number of advantages over thermal processes as will be discussed later in chapter two [8] .

Nowadays almost 60% of the feed water used in desalination plants are sea water (Figure I.3) and 60%of desalinated water is producedby membrane technology also called Reverse Osmosis (RO) technology which is better and more efficient than thermal desalination for treating this type of water [6]. So, membrane technology market is directly proportional to the feed water and hence it is increasing over the thermal technology as shown in Figure I.4 as well [6].

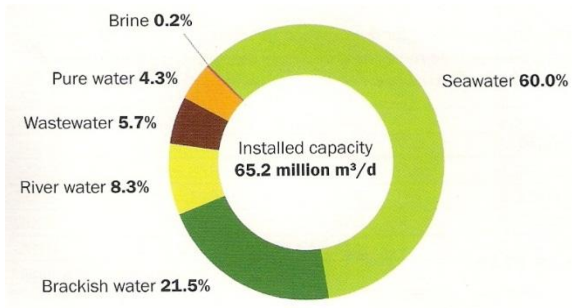

Figure I.3 globally installed capacity by feed water (left)[6]

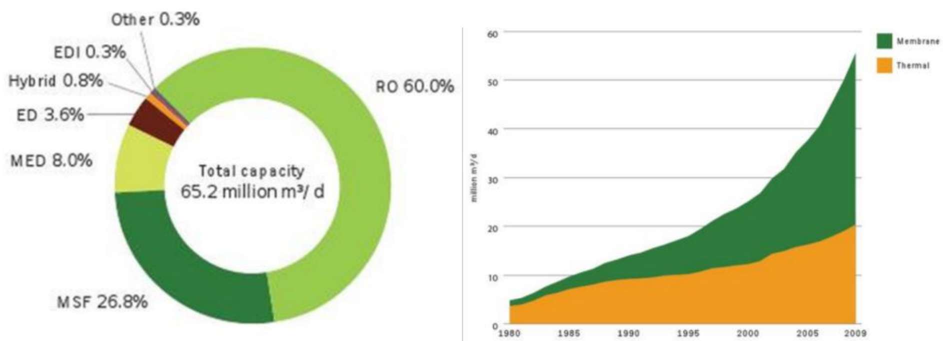

Figure I.4 Global capacity of water desalination by technology[6]

1.2 Research objective

Over the past 25 years desalination plants all over the world were moving toward membrane technology mainly RO technology because of its advantages compared with the thermal processes [4]. Different types of membranes are being developed commercially depending on the process and the type of feed water that they will treat. The variations include different manufacturing material, pore size, module shapes and configuration, hydrophobicity, etc.

The research work done in this thesis focuses on two types of membranes that are Microfiltration (MF) and Ultrafiltration (UF) membranes which are used in pre-treatment of Sea Water Reverse Osmosis (SWRO) plants. The research will include various types of MF and UF membranes and spot the light on how to maintain the membrane productivity and the filtrate quality. Different techniques are being proposed such as using different MF/UF membrane pore sizes and with different configurations. Also the experiments were conducted with/without using coagulant with different concentrations. The properties and quality of permeate are studied and analyzed in order to identify and propose the best membrane type and configuration to be used in SWRO pretreatment processes. This research is a short term experiment and start-up phase that will be continued by a long term study carried by a PhD student, Muhannad Alghamdi.

1.3 Thesis Layout

The content of this thesis has been prepared starting by background about seawater desalination technologies with a focus on RO membrane pretreatment technology. The literature review presents background knowledge about conventional and membrane pretreatment processes and compare between them. It starts by chapter II which gives an overview about MF/UF membranes properties such as manufacturing materials, pore sizes, applications, shapes, hydrophobicity and configuration. Then it will focus on membrane applications for SWRO pre-treatment and the types of coagulants used and required concentration, then comparing it with the conventional pre-treatment. Then several case studies of existing commercial plants using MF/UF as pretreatment for SWRO will be presented.

Chapter III includes the experiment details and procedures, methods used for analysis and results. It starts by identifying the location of feed water source and its parameters. Then it explains the experimental design, equipment used and processing. A detailed explanation about the different membranes properties used in the experiment is presented. Also, it will include explanation about the coagulant type and concentration used. Results and analysis of the water chemical and physical parameter and findings are discussed at the end of this chapter. Chapter IV shows the results obtained by each configuration and discuss them. All data analysis and comparison between different membrane configuration systems have also been explained in this chapter. Finally in chapter V conclusions and recommendations of this research are drawn.

Chapter II

2.1 SWRO Pre-treatment Technologies

Proper pretreatment is a key factor for a successful desalination plant operated with RO technology [7]. Studies show that CAPEX and OPEX for pretreatment system can reach up to 50% of the total desalination plant cost [10]. Two major technologies are used for pretreatment the conventional pretreatment and using low pressure membrane for SWRO pretreatment.

2.1.1 Conventional pretreatment

The conventional or traditional pretreatment which is mainly sand filter designed in a deep bed consisting of several layers of gradually decreasing in size from gravel to anthracite. The suspended particles are removed while moving downstream through the media. Other techniques are involved in the process to improve the filtration and the product water quality such as coagulation, flocculation and sedimentation and the figure below shows an example of typical conventional pretreatment process [11]. This conventional pretreatment can remove particles as small as 10-20 μm sizes, but with the coagulants it can reach up to 1μm size [12].

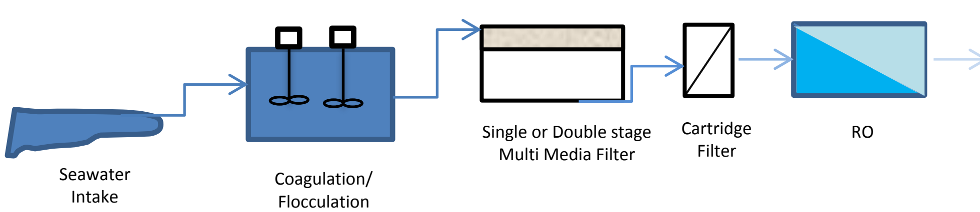

Figure II.1 Typical example for conventional pretreatment

The feed water that is applied to RO after pretreatment should have some characteristics and quality that cannot be guaranteed to be achieved by the conventional pretreatment. The silt density index (SDI) of value 5 percentage per minute as the maximum recommended value for some and not the entire RO manufacturer while for all others it should be below 3 [12, 13]. SDI values achieved by conventional process ranges between 3 to 5 [12].

2.1.2 MF/UF Pretreatment

The use of membrane technology to produce water with different quality is being a widely used for different water sources, i.e. surface water, brackish water and seawater [14]. Unlike conventional pretreatment the use of membrane technology removes particles smaller than 0.1 μm sizes and SDI value are often less than 3, so it is considered ideal for SWRO pretreatment [12]. Nowadays using membrane processes for seawater desalination is spreading globally and replacing the thermal process that used to be the main technique used for seawater desalination. Figure II.2 shows that in the last 25 years there is an increase of using RO globally replacing the other technology used for desalination. However, while about 50% of the global desalination capacity is being produced in the MENA countries, studies done in 2002 show that RO desalination accounts for only 10% of it. That is because in order to increase the fuel efficiency it has been used for cogeneration of electricity and thermal desalination [4, 14].

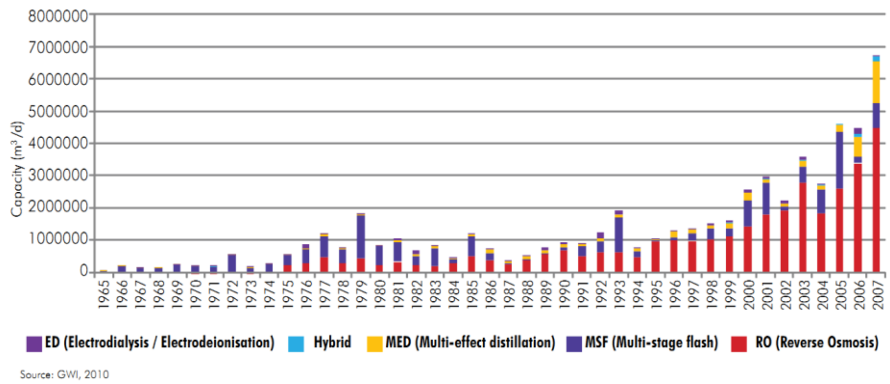

Figure II.2 Global contracted capacity by technology [4]

Recently, in 2010, another study has been done by Global Water Intelligence showing that there is a dramatic increase in using RO membrane for desalination in MENA region as shown in Figure II.3.

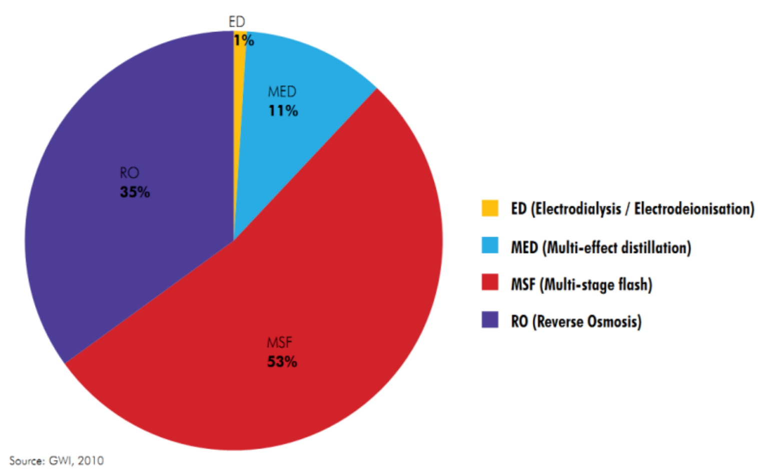

Figure II.3 Cumulative contracted capacity by technology since 1944 in the MENA region [4]

This increase of use of RO technology especially SWRO is compatible with the increase in research and development in order to apply the optimum pretreatment technology. Only since 2006 the use of MF/UF membranes as pretreatment for SWRO is being significantly globally accepted technology (Figure II.4) for the new desalination plants and even replacing the conventional sand filtration pretreatment process [15]. This is because RO membranes in general have some limitations regarding turbidity, temperature 45^{0}C at maximum, pH value range between 2 – 10 and most importantly the SDI must be below 3 (percentage per minute).

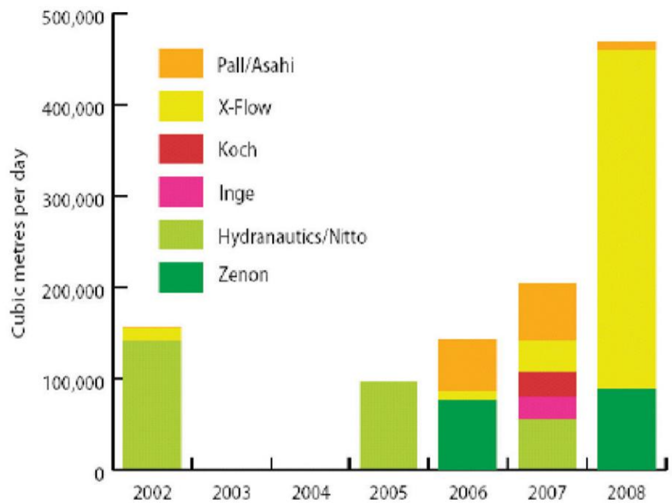

Figure II.4 UF/MF used in pre-treatment for seawater desalination, annual capacity by manufacturer [15]

Studies and experiments have shown that using MF/UF for pretreatment guarantee a better and more consistent water quality especially turbidity and SDI when compared with the conventional, e.g. coagulation/sedimentation and sand filtration. In addition, the high and constant quality of MF/UF permeate compared to the conventional pretreatment means higher flux and recovery rate for the RO membranes and thus lower the cost of the whole desalination plant [7]. Table II.1 summarizes the most significant differences between conventional and MF/UF pretreatment technologies [16].

Table II.1 Comparison between conventional and MF/UF pre-treatment technologies[16]

Parameter	Conventional pre-treatment	Membrane pre-treatment	Benefits
Capital cost	Cost competitive if compared to MF/UF	Slightly higher than conventional pre-treatment and costs continue to decline as developments are made	Capital costs of MF/UF could be 0–25% higher, whereas life cycle costs using either of the treatment schemes are comparable
Energy requirements	Using gravity flow, it requires less energy	Higher than conventional.	MF/UF requires pumping of water through the membranes. This can vary depending on the type of membrane and water quality
Foot print	Calls for larger foot print	Significantly smaller foot print	Foot print of MF/UF could be 30–50% of conventional filters
Chemical costs	High due to coagulant/flocculant and process chemicals required for optimization	Chemical use is low, dependent on raw water quality.	Less chemicals
RO capital cost	Relatively higher since RO operates at lower flux	Higher flux is logically possible resulting in lower capital cost, which may allow higher recovery	Due to lower SDI values, RO can be operated at 20% higher flux if feasible, reducing RO capital costs
RO operating costs	Relatively higher costs since the high potential of membrane fouling will result in higher operating pressure. Also may result in frequent cleaning of RO membranes.	Lower RO operating costs are expected due to less fouling potential and longer membrane life	The net driving pressure is likely to be lower if the feed water is pre-treated by MF/UF. Membrane cleaning frequency is reduced by 10–100%, reducing system downtime and prolonged element life.

2.2 Overview of MF/UF Membranes

2.2.1 Filtration mechanism

The membrane filtration mechanism depends on the driving force by the pressure difference for the separation and filtration process [17]. In 1960s, this technique has been adopted and used in several fields such as chemical industries, pharmaceutical production and for water and wastewater treatment after the two scientists Loeb and Sourirajan had innovated a membrane module that can be used in industrial scale [18]. Membranes in term of pore size are divided into four main categories that are microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO). The pore size ranges from several micrometers as the case of MF to several nanometers size as the case of UF and even smaller than nano-scale as in NF and RO as shown in Figure II.5 [18]

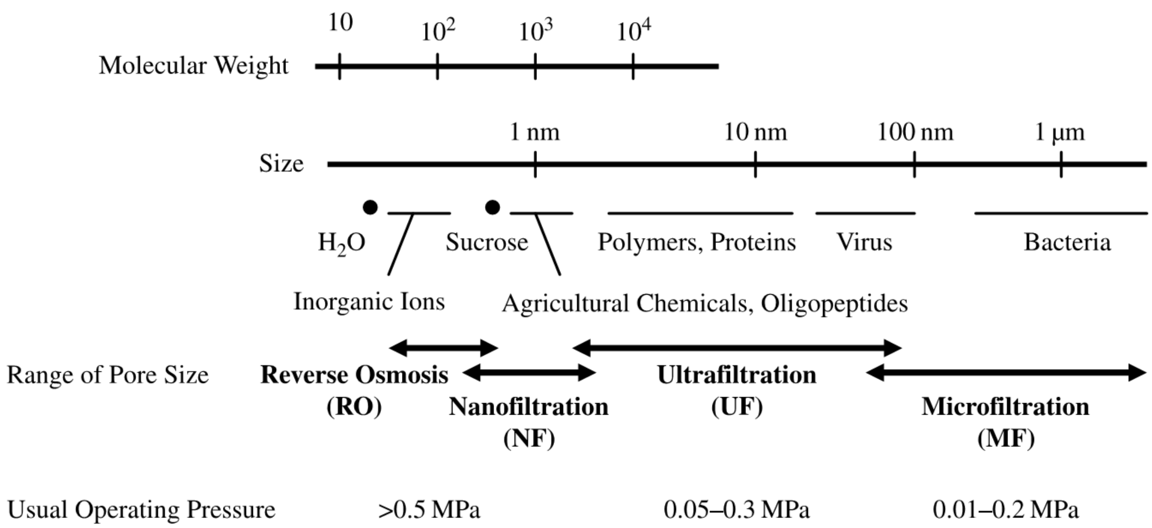

Figure II.5 Pore size range of various membranes process [18]

However this research will focus on MF and UF membranes with pore sizes that ranges between 0.05 to 5 µm and 1 to 100 kDa, respectively [19].

2.3 MF/UF membrane Properties

2.3.1 Material

UF/ MF membranes can be divided into two main categories. The first category includes membranes that are made from organic polymers such as polyethylene (PE), polyether sulfone (PES) and Polyvinylidene fluoride (PVDF). While the second category contains membranes made form inorganic materials such as ceramic, glass and metals [18, 20].

Organic polymer membranes are most commonly used for UF/MF application while the research is still being done for the inorganic material [21]. Organic membranes also are divided into two other groups hydrophobic group and hydrophilic group [20]. Hydrophilic membranes are the one that are made from cellulose or its products and many of the membrane manufacturers still use this material to produce MF and UF membranes. However the main disadvantage of cellulose acetate is that it is sensitive to acid and alkaline hydrolysis and temperature. Polyethersulfone (PES) (used in this research) is considered a hydrophilic and also commonly used for UF membranes [19]. While hydrophobic membranes such as polyethylene (PE) and polyvinylidene fluoride (PVDF) are used frequently for manufacturing MF membranes [22]. Advance technologies are used to blend hydrophobic with hydrophilic polymers to modify them to reduce membrane fouling [14].

Inorganic membranes also called ceramic membranes, examples of manufacturing materials, are found on Table II.2. Inorganic membranes are characterized by their exceptional stability at high temperatures (over 100^0C) and extreme pH values [19]. However, the main disadvantage is that they are mechanically weak on another word brittle [19].

Table II.2: Materials for MFand UF Membrane Fabrication [1]

Membrane	MF	UF
Organic		
Acrylonitrile polymer	✓	✓
Cellulose acetate (cellulose-2-acetate, cellulose-2,5-diacetate, cellulose-3-acetate)	✓	✓
Cellulose nitrate (CN)	✓	
Mixed cellulose esters	✓	
Regenerated cellulose	✓	✓
Nylon	✓	
Polyamide (aromatic polyamide, copolyamide, polyamide hydrazide)	✓	✓
Polyacrylonitrile (PAN)		✓
Polysulfone (PS)	✓	✓
Hydrophilic polysulfone		✓
Polyelectrolyte complexes		✓
Polyester		✓
Polyether sulfone (PES)	✓	✓
Polycarbonate (track etched)	✓	✓
Polyethylene terephthalate (PET) (track etched)	✓	✓
Polyimide		✓
Polyethylene (PE)	✓	
Polypropylene (PP)	✓	
Polytetrafluoroethylene (PTFE)	✓	
Polyvinylidene fluoride (PVDF)	✓	✓
Polytetrafluoroethylene (Teflon)	✓	
Polyvinylchloride (PVC)	✓	✓
Inorganic		
Alumina		✓
Aluminum oxide (Al_2O_3)	✓	
Zirconia (ZrO_2)−carbon		✓
Zirconia (ZrO_2)−polyacrylic acid		✓
Titania	✓	✓
Ceria (CeO_2)	✓	
Glass (SiO_2)	✓	✓
Stainless steel	✓	
Palladium (PD) and its alloy	✓	

2.3.2 Pore size or molecular weight cut off (MWCF)

Both expressions are used interchangeably to define the size of pores of the membrane but MWCO is used to define the size of smaller pores. The MWCO is a parameter that depends on the performance and it is defined by measuring and knowing the MW of the solute that has been 95-98% rejected by the membrane [23]. On the other hand, pore sizes of the MF membranes ranges between 0.05 - 5 µm but it is interconnected pores meaning that it is not one pore with one diameter through both surfaces of the membrane. On the other hand, UF membranes pores ranges from 1 to 100 kilo-Dalton or it can be said it is around 5 to 100 nm [19, 22]. Figure II.6 and Figure II.7 below shows the different pores and pore sizes by SEM images for inner and outer surfaces of the membranes used in this research [24].

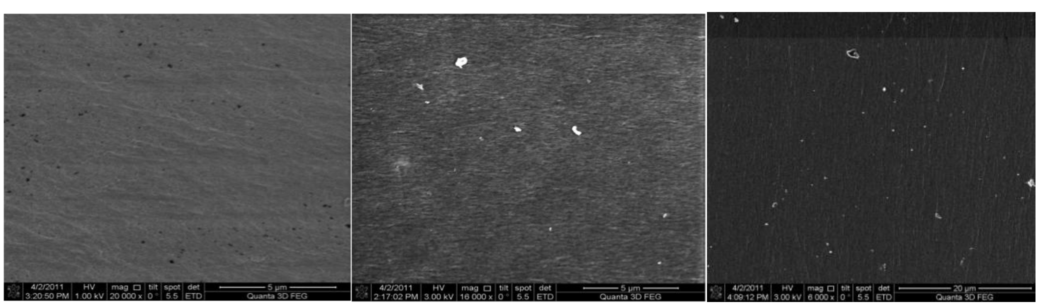

Figure II.6 SEM image shows pores sizes of the inner face of inside-out different membranes MF 0.1um, UF 100kDa and UF 50kDa (left toright)

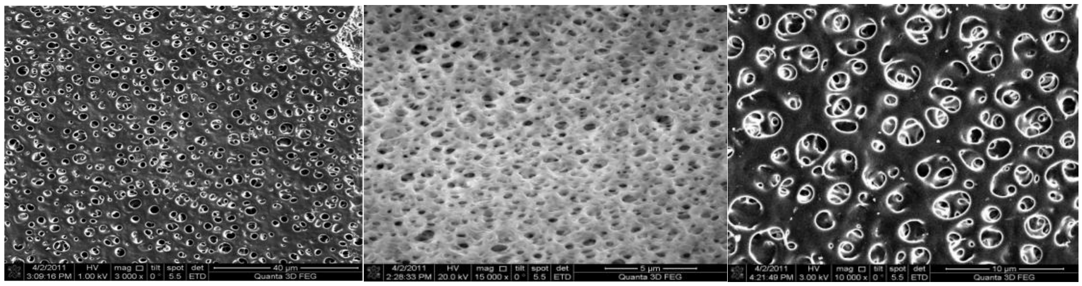

Figure II.7 SEM image shows different pore sizes of the outer face of inside-out MF 0.1um, UF 100 kDa and UF 50 kDa (left to right)

So, MF/UF are basically used as a replacement for conventional filtration but with smaller scale and same productivity of bacteria and suspended solids removal [25]. However UF membranes have smaller pores allowing it to be used for removing of turbidity and small particulate matter such as viruses, microorganism and any substances with MWCO between 10 – 500 kD as shown in Figure II.8, which shows different sizes of matters that can be removed by different membranes [22, 26]. However, MWCO of any membrane does not guarantee that it will reject all compounds within the specific size but there are some other factors such as the shape of the molecule, polarity, and membrane/solute interaction which affect the rejection [26]. Moreover, membrane surface characteristics such as porosity of the surface and distribution of the pore sizes may also influence the apparent particles size and so the rejection [18].

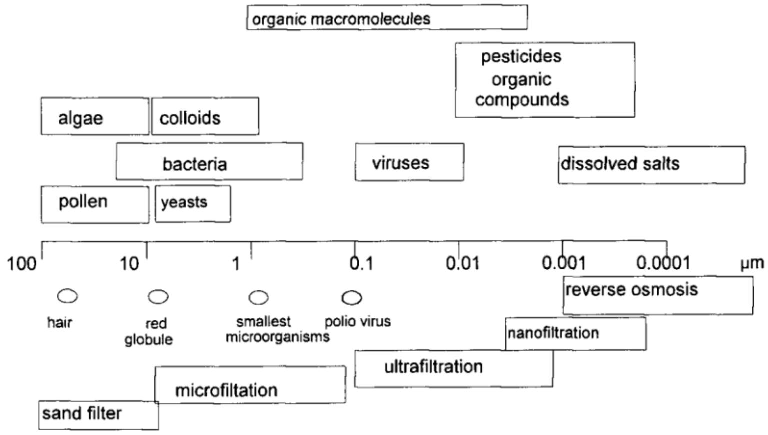

Figure II.8 Classification of the pressure driven membrane filtration processes and conventional sand filtration based on the size of particles and molecules removed

2.3.3 Porosity

Also called pore density, is defined as the volume of the pores divided by the volume of the membrane or the material. As shown in Figure II.9 the porosity can be different for the same pore size of a membrane and it is measured by the same technique used to measure the pore size distribution such as scanning electron microscopy (SEM) and transmission electron microscopy (TEM) [19, 27].

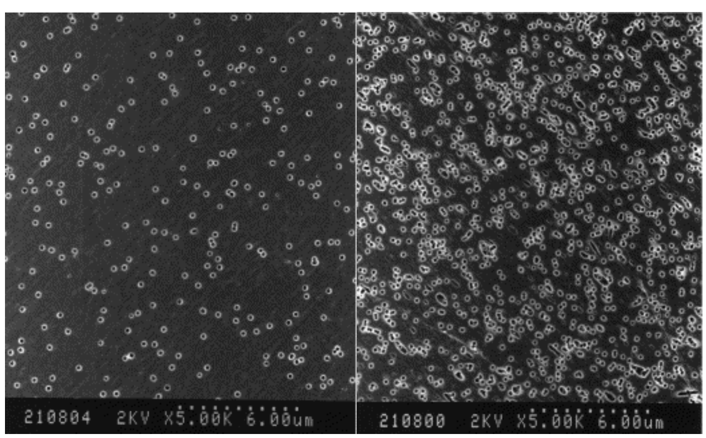

Figure II.9 Two types of 0.2 μm membranes with difference porosity [27].

2.3.4 Membrane permeability

Or inverse of membrane resistance and it is the ratio of the Trans-Membrane Pressure (TMP) to the permeate flux (J) [28]. Darcy's law is used to describe the permeability and it uses most of the factors that affect it, that is:

$$J = \frac{TMP}{\mu\, R_m}$$

Where R_m represents the membrane resistance (m^{-1}) and μ the viscosity of the water which decrease with temperature and increase with higher solute concentration. Engineers and researchers always try to develop a membrane with high permeability which gives a higher flux so it is more economical, but it is not always the case because high flux causes high polarization concentration and high fouling rate which is not economically efficient [29, 30]. In addition, beside transmembrane pressure the permeability depends on many other factors such as the membrane history and age, filtration time and temperature of the feed [31].

2.3.5 Module configuration or Pressure configuration

The smallest area in which the membrane is being packed is called module [20]. Different modules are available commercially but all of them depend on one of two configurations: 1) flat or 2) tubular. While plate-and-frame and spiral wound shown on Figure II.10 are flat membranes [20, 32].

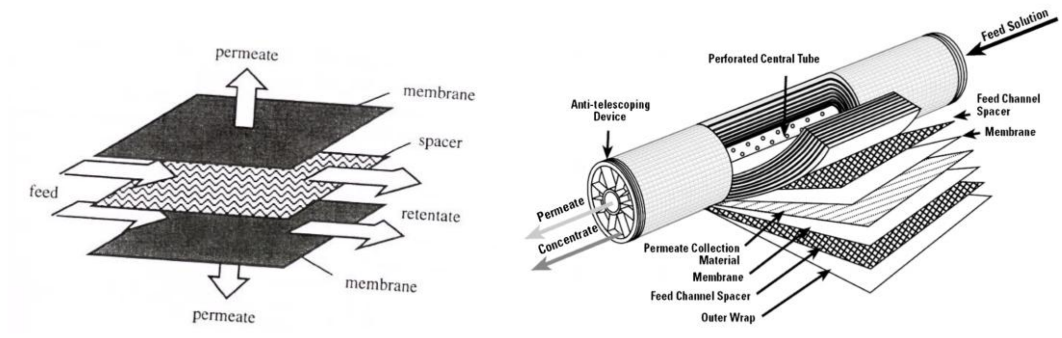

Figure II.10 on the left Schematic diagram for a plate and frame module, and in the right, a schematic diagram for the spiral wound module [20, 32]

However the hollow fiber and tubular type membranes as shown in Figure II.11 are tubular. Out of all of these modules the hollow fiber module can provide the largest possible packed membrane area per unit volume that means it is the most economical and it is the most common configuration for UF and MF membranes used for water treatment [19, 33]. In this work only hollow fibre membranes provided by different manufacturers have been used.

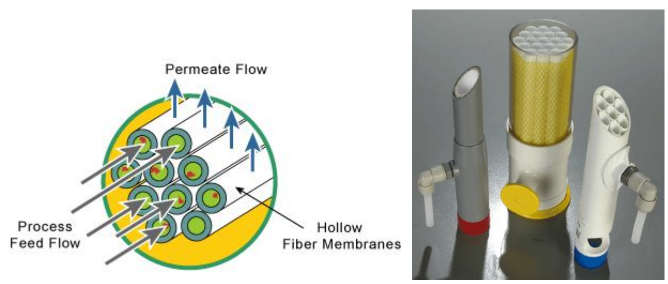

Figure II.11 the left schematic diagram for a hollow fiber membrane and the right shows tubular type membrane [33]

Hollow fiber membranes have the smallest tube diameter generally 0.5-1.5 mm diameter (< 5mm) and they are packed in the module in huge amounts as shown in Figure II.12 [19, 34]. Another very important advantage of using this configuration for water pretreatment is that it does not need an extensive pretreatment since it can be backwashed by reversing the flow direction and flushed the cake layer that forms on the membrane surface [35].

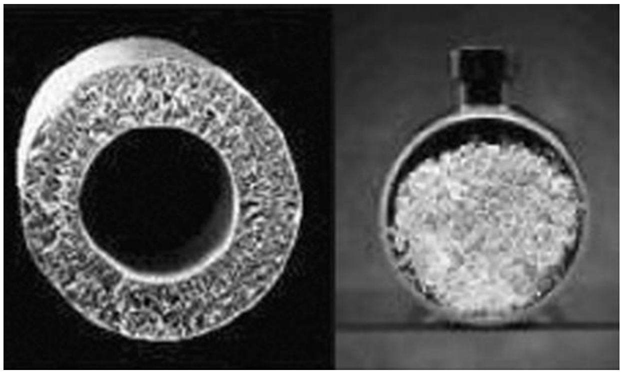

Figure II.12 Couple of thousands of hollow fibers membranes packed in module [34]

Two different modes are used for the feed water that passes through the membrane inside-out or outside-in simply described on Figure II.13below. In outside-in mode the feed water surrounds the membranes and permeates are collected inside the fibers. This design is better than inside-out because it has a larger contact surface area between the membrane and the feed. While in the inside –out scheme the feed flows inside the hollow fibers and the permeate is collected outside the fibers [36]. This system has better hydrodynamic flow than the out-in mode[26].

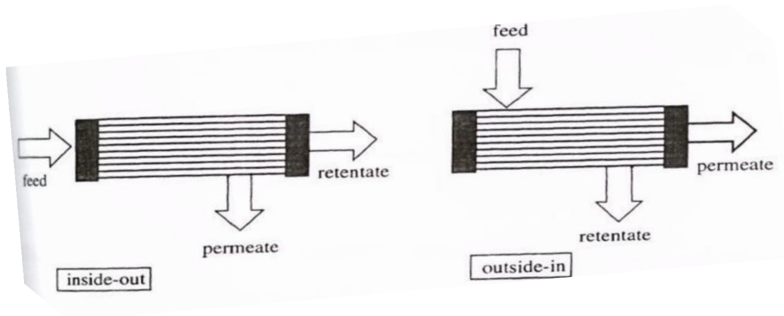

Figure II.13 Hollow fiber module of the Inside-out (left) and outside-in (right)

2.3.6 Process configuration

Mainly two system configurations are used: dead end and cross flow systems [20]. It is mainly the relation between the direction of the feed water and the surface of the membrane. Both modes are differing mainly in filtrate rate, recovery, flux and permeate quality.

2.3.6.1 Dead End Filtration mode

It is the most used configuration in water desalination plants [19]. In this schematic Figure II.16 the recovery is 100% but some of this portion is used for backwashing [5-15%][19, 20]. So, in dead end mode:

$$Q_{feed} = Q_{permeate}$$

However, more solids build up on the membrane surface and fouling cake layer is created as shown in Figure II.14 [20].

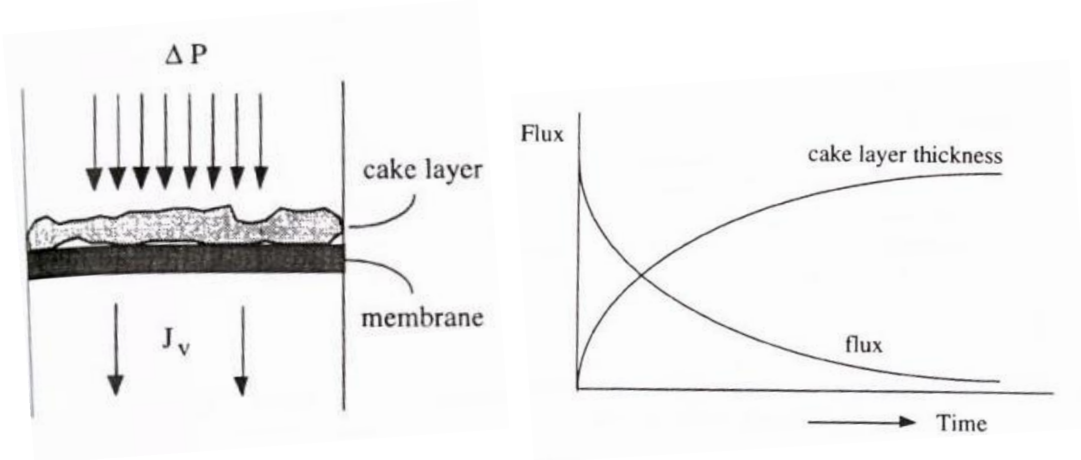

Figure II.14 Flux decline vs fouling increase in Dead end filtration mode [20]

So, this mode requires backwashing more frequently than cross flow filtrations [37]. Additionally, after some time the TMP becomes higher and the backwash gets more difficult meaning it needs additional membrane cleaning and that is called chemical enhanced backwash CEB as shown in the Figure II.16 [37].

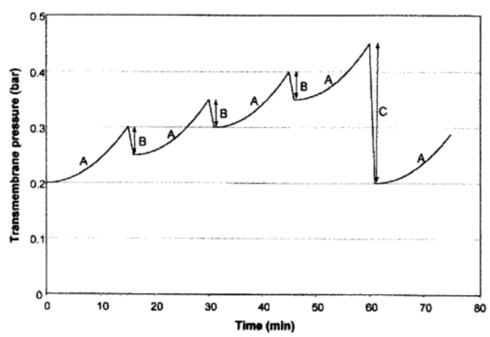

Figure II.15 A explains TMP changing with time, B after Backwash and C represents CEB effect [37]

Nowadays, most desalination plants using MF/UF membranes are using dead-end mode because it requires fewer energy compared to the high velocity of the feed water pumped required in cross flow to prevent fouling which result in increased head loss and energy consumption [20, 37].

2.3.6.2 Cross flow filtration mode

In contrast to the dead end, in cross flow mode water flows parallel to the membrane as shown in Figure II.16. This mode is used mostly in industrial applications since it has a less tendency to foul compared to the dead end [20]. However, the cross flow scheme is different since:

$$Q_{feed} = Q_{premeate} + Q_{concentrate}$$

This is preferred in some industrial applications since the solids are flushed continuously with the concentrate resulting in a longer life for the membrane and of course less backwashes as well [20]. Another advantage of this system is that it can be converted to a dead end mode by closing the discharge valve [37].

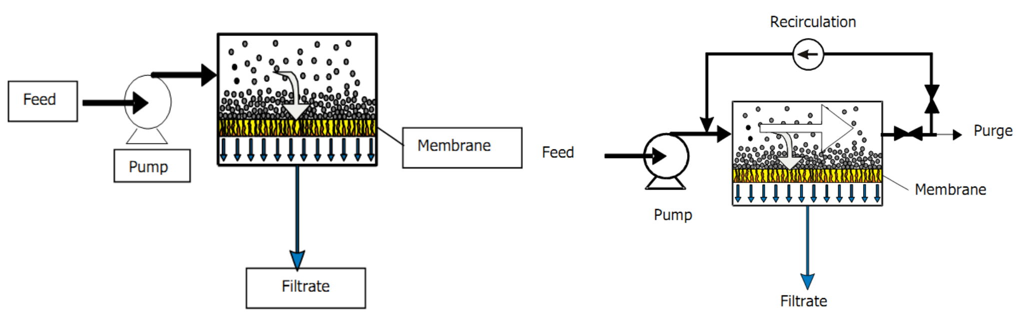

Figure II.16 Modeling of the two basic membrane operating modes (Left -Dead end and Right-Cross flow) [38]

2.4 Fouling:

Fouling is strongly related to the flux either by decreasing the flux in case of constant pressure processes or by increasing the TPM in case of constant flux [39]. It happened in two different phases:

1- Reversible fouling: accumulation over a filtration cycle or between cleaning intervals.

2- Irreversible fouling: over the life of the membrane module and this one takes several forms: A- particulate/colloidal fouling. B- Organic fouling. C- Biofouling: first by attachment then by formation of biofilm [40].

2.5 Pre-treatment strategies and applications (case studies):

This section includes two tables (Table II.3 and Table II.4) that summarize and compare between SWRO plants that use either MF/UF membranes technology or conventional pre-treatment technology. Several case studies have been reviewed and analysed. Some of them evaluated only one of the two technologies. However, other papers evaluated and compared the two technologies in the same study. These studies have been highlighted with the same colour on tables Table II.3 and Table II.4.

Table II.3 Conventional pre-treatment case studies and analysis. Note/ same colors on the two tables indicate the same research done for both technologies.

Ref.	Case Name	Raw Water Source	Source Water Parameters	Process Design	Coagulant	Permeate Parameters	Remarks
[41]	Jeddah SWRO plants, 1989	Deep Red Sea water disinfected by NaClO	SDI=5.5 to 6 and TDS= 43,300 mg/l	Dual media filter (DMF) (anthracite and sand) flowed by 10 µm cartridge filters	0.3 mg/l of FeCl3 mixed with 0.1mg/l of polyelectrolyte	SDI < 4.0	Coagulants prevent membrane degradation and control quality of the varaible SDI
[42]	Doha Research Plant, Kuwait	Surface Arabian Gulf seawater	TDS of 47,000 mg/L and SDI_{15} > 6.5	FeClSO4 flocculation and media filter with various grain size: silica sand range (0.7–1.2 mm, 1 m high) and anthracite ranges (1.4–2.5 mm, 0.7 m high).	No	SDI value of 3.6.	Several failures caused by climatic conditions and dosing rate of FeClSO4 and other.
[43]	Persian Gulf and Indonesia-1	Persian Gulf	SDI_{10}= .45, turbidity .07NTU, algae bloom and hydrocarbon pollution	DAF with double filtration including addintion of two coagulants	FeCl3 and polymers	SDI=1.8 to2.9,UV removal= 20–30%	Results in efficient feed water for RO
[43]	Persian Gulf and Indonesia-2	Persian Gulf	TDS=25–50 g/l, turbidity 5–20 NTU, pH=8–8.5	DAF unit followed by polishing horizontal filter.	FeCl3 and polymers	Turbidity= 0.25 NTU and SDI< 1.5	The system max. recovery of 35%
[13]	French Institute of Marine Research	Seawater	Turbidity 0.5–4 NTU,TOC= 2.7 to 6.1mg/l and SDI= 6.1 to 6.4, pH 8, SS= 10-20 mg/L, T= 9 to 25 °C	Coagulation followed by sand filtration (10 µm)	PAC	SDI= 5.8 - 5.9	The permeability of the RO membranes has decreased by 28% during 30 days.
[7]	ONDEO Services, Gibraltar	Gibraltar seawater	Conductivity=48.7 mS/cm and SDI=13-15 and algea bloom	Organic coagulant, three DMF then 10µm cartridge filtrs	Organic	SDI = 2.7 - 3.4	See the other table
[44]	Singapore SWRO plant	Seawater	SDI= 6.1–6.5,TSS=6 mg/L	Coarse screens then Single Media Filter and 3 stages of 10,5 and 1µm polishing cartridge filters	Polymeric	SDI= 4 on average	See the other table
[45]	Ashdod Plant	Mediterranean surface seawater	Turbidity=1-10NTU,TDS=40,500 mg/l, SDI>6.5 and SS=2–14 mg/l	Settling and coagulation then media filtration	0.3–0.7 mg/l ferric salt	Turbidity= 0.1–0.2 NTU, SDI=2.6 to 3.8	See the other table

Table II.4 MF/UF pretreatment case studies and analysis. Note/ same colors on the two tables indicate the same research done for both technologies.

Ref.	Case Name	Raw Water Source	Source Water Parameters	Process Design	Coagulant	Permeate Parameters	Remarks
[13]	French Institute of Marine Research	Seawater	Turbidity 0.5–4 NTU,TOC= 2.7 to 6.1mg/l and SDI= 6.1 to 6.4, pH 8, SS= 10-20 mg/L, T= 9 to 25 °C	Coagulant and dead-end hollow fiber UF membrane (pore size of 0.01 µm)	PAC	SDI= 1-2, turbidity< 0.1NTU, SS < 0.01 mg/L	Constant permeability for the RO during 20 days trial
[7]	ONDEO Services, Gibraltar	Gibraltar seawater	Conductivity=48.7 mS/cm and SDI=13-15 and algea bloom	200 µm pre filter and 100kDa UF membrane. Then 5 mg/L of free chlorine was added	Organic	SDI < 0.8	Fouling removal was more efficient with UF than with conventional pre-treatment.
[44]	Singapore SWRO plant	Seawater	SDI= 6.1 to 6.5,TSS=6 mg/L	Direct flow through 0.1µm MF membrane flowed by 0.01 µm UF dead end mode	Polymeric	Turbidity=1.5-3 NTU, TSS=1.3 mg/L, SDI=2-3	Flux increased when SDI approx.3
[45]	Ashdod Plant	Mediterranean surface seawater	Turbidity=1-10NTU,TDS=40,500 mg/l, SDI>6.5 and SS=2–14 mg/l	50µm screen filter and followed by UF filtration using coagulant	0.3 mg/l ferric and 20mg/l hypochlorite	Turbidity=0.09–0.16 NTU, SDI=2.1 to 3	Seasonal storm increases TSS value then UF becomes preferable
[46]	Addur Desalination Plant	Gulf seawater	SDI=15–19	Pre-chlorination followed by sand filtration then spiral wound UF membranes	1mg/l $FeCl_3$ in winter & 2mg/l in summer		Coagulant improves the filtrate quality

By comparing these two systems it is obvious that MF/UF membrane pre-treatment has advantages and benefits over the conventional one for the SWRO desalination plant and these results can be summarized in the following points:

1- Higher flux and recovery for RO can be achieved by MF/UF pre-treatment.
2- Minimizing the footprint required for the plant.
3- Increase the life time of RO membranes, hence reduce the cost.
4- Can treat all kind of water even poor quality sources with the same efficiency.
5- Guarantees the quality of the feed water for RO membranes.

Chapter III

3.1 Materials and Methods

The purpose of this research was to quantify the performance of low pressure membranes used as pretreatment for SWRO these are 0.1µm MF, 100 kDa UF and 50 kDa UF membranes, to filter the Red Sea water. All the experiments were done on dead-end mode since it is the mostly used mode for desalination pretreatment [37]. In addition, two process configurations have been tested namely constant pressure, variable flux and constant flux, variable pressure vs. time.

Initially, the experiment was done on the 0.1µm MF membrane with the two process configurations with and without coagulant injection. Ferric Chloride ($FeCl_3$) was injected at different concentrations, 1mg/l, 2mg/l and 3mg/l. Then a concentration of 1mg/l and 2mg/l was tested on the 100 kDa UF. However no coagulation addition was used for the 50 kDa UF membrane. The following Table III.**1** summarizes the different design processes done in this research.

Table III.1 The different coagulation dosing concentrations used in the different experiments

		$FeCl_3$ Coagulation Addition			
	Configuration	**No addition**	**1mg/l**	**2mg/l**	**3mg/l**
0.1 µm MF	Dead End	✓	✓	✓	✓
100 kDa UF	Dead End	✓	✓	✓	x
50 kDa UF	Dead End	✓	x	x	x

The goal of the work is also to test the permeate water quality and insure that it is filterable for the RO feed. Standard water quality parameters were assessed and measured for all permeate and were compared in order to know which configuration is best in terms of turbidity and TOC removal and SDI_{15} reduction.

3.2 Source Water Details

The water samples used in the experiments were taken from the deep Red Sea water. The red sea is located on the west side of King Abdullah University of Science and Technology (KAUST) University campus which is located in the western region of Saudi Arabia about 100km north of Jeddah city. The sample were taken from a point source that is about 2,43 km west of KAUST campus as shown in Figure III.1. The coordinates of the sources are: N 22°18'05.8" E 39°04'00.8" (Google Maps).

The point of choosing that source from the deep and not the shore is to try to mimic real desalination plant raw water. Also, other samples were taken from different locations on the shore and the water quality was poor meaning it has a high turbidity and SDI values.

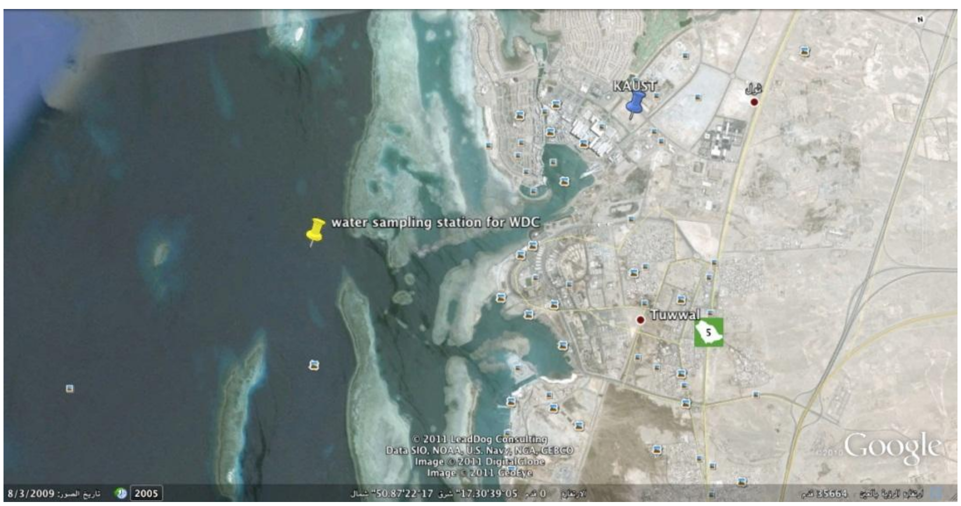

Figure III.1 Google earth image describes the sources water used in the experiments

The following Table III.2 summarizes the analysis of source Red Sea water:

Table III.2 Experiment Red Sea water analysis

PH	7.8 - 8.2
Turbidity (NTU)	Approx. = 0.2
Conductivity (mS/cm)	60.5
TDS (g/l)	40
TSS (mg/l)	0.0188
SDI_5 (%/min)	11.9
TOC (mg/l)	1.042
DOC (mg/l)	1.176

3.3 Membrane Modules Details and Specifications

A total of three different membrane units are used in this experiment. All of them are hollow fiber membranes which are made from Polyethersulfone (PES) [38]. PES material is preferred for this application since it is neither extremely hydrophilic nor extremely hydrophobic and it can be blended with other polymer to increase or decrease its hydrophobicity as needed. Also, hollow fiber membranes are dominated for drinking water treatment applications [38]. The only difference between the three membranes is the pore size and the following Table III.3 shows data about the membranes pore sizes.

Table III.3 Pore sizes details for the membranes used in the experiment

Membrane Type	Pore Size (µm)	Molecular Weight Cut Off (MWCO) (kDa)
1. Microfiltration membrane	0.1	---
2. Ultrafiltration membrane	Approx. 0.02	100
3. Ultrafiltration membrane	Approx. 0.01	50

In addition, all the membranes work on inside-out mode so it has a very low volume of feed water compared with the product outside the fibers which makes it economical for backwashing since it requires shorter intervals. Additionally, they are made in multipore fibers meaning each fiber contains seven pores to minimize the possibility of breaking the fibers. Figure 3.2 shows the multi pores in one fiber and direction of water flow as well as the inner face of the three membranes used in the experiment. Also, more figures for the inner and outer faces of the membranes are presented in chapter two Figure II.6 and Figure II.7.

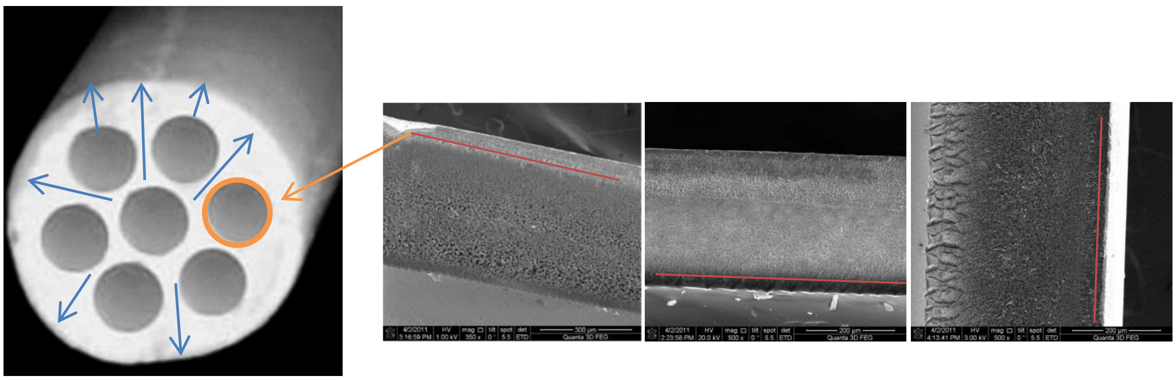

Figure III.2 inside-out multi pore hollow fiber membrane, the inner face of 0.1 MF (left), 100kDa (middle) and 50kDa (right) [24]

All modules were received from the manufacturer in sealed and vacuumed plastic wrapping and it is filled with non-toxic solution of potable water, glycerin and sodium bisulfite [74, 25:25:0, 75 wt%] in the pores of the membranes in order to prevent dehydration and bacterial growth. Prior to use, several rinsing procedure with RO water for 1 hour with different water pathways in the module were performed in order to make sure that all the residuals are flushed out from the pores before use. The same procedure was performed in all the membranes. After membranes being used, they were backwashed with RO water then rinsed with a 0.75% sodium bi-sulphite ($NaHSO_3$) then submerged in this solution and kept in a container as shown in Figure 3.3.

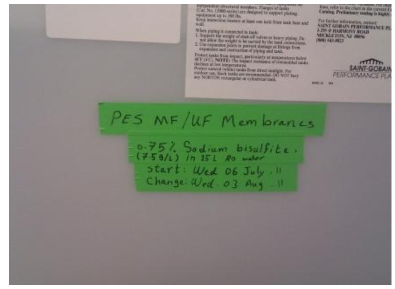

Figure III.3 Membranes conservation between two experiments (submerged in 0.75 sodium bi-sulphite)

The membranes are tolerant to chlorine up to 200 mg/l and also can tolerate pH range from pH =1 to pH= 13 which gives a good cleanability for organic and inorganic matters. Table III.4 below outlines more details of the membrane properties used in the experiment.

Table III.4 Membranes technical information as given by the manufacturer

Properties	**Range**
Membrane surface area	**0.1 m^2**
Flux rate	**60 – 180 lmh**
Backwash range	**230 – 300 lmh**
TMP for filtration	**0.1 – 1.5 bar**
TMP for backwash	**0.3 – 3 bar**
Temperature range	**0 – 40 ^{0}C**
pH tolerance	**1 – 13**
Free chlorine tolerance	**Max. 200 mg/l**

3.4 Experimental bench scale apparatus

The first step of this research project was to determine the configuration of the bench-scale membrane pre-treatment system. Figure III.4 shows the process flow diagram that has been designed and built in the lab.

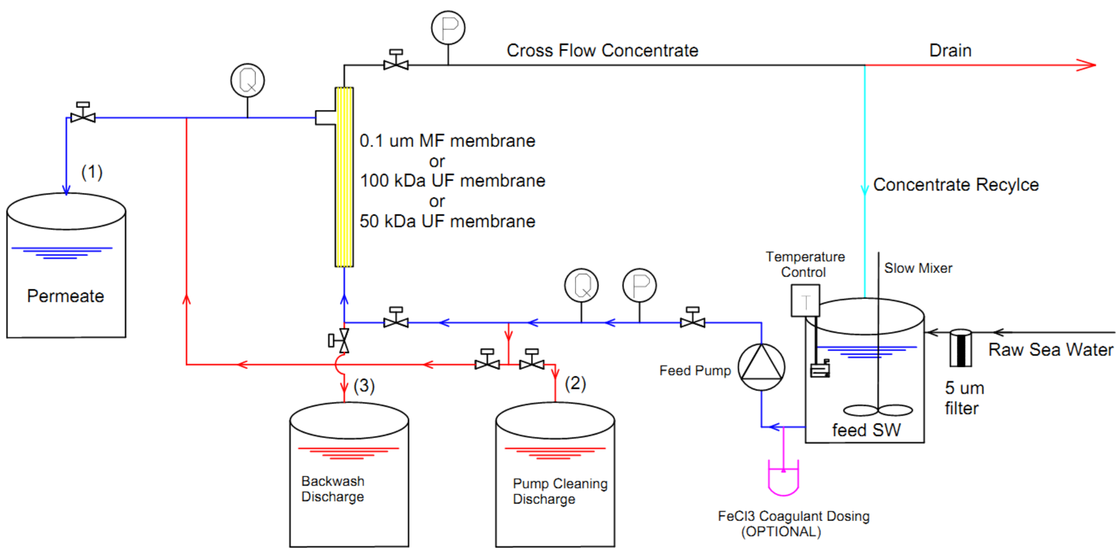

Figure III.4 Bench scale membrane pretreatment system process Flow Diagram

3.4.1 Process flow diagram

The raw water tank has a capacity of 20 US Gallons (approx. 75.7L) and equipped with a submerged pump. When it is filled with sea water, the submerged pump at the bottom of the tank push the raw water to pass through a 5µm cartridge filter and then fill the feed tank. The point of having 5µm cartridge filter is to assume the removal of debris and suspended solids in the feed water which might harm the membranes and affect its efficiency. The feed tank has the same capacity of the raw water tank (approx. 75.7L) and contains all the sea water before being pumped to the membranes. The water in this tank was kept in a slow motion status by means of a mixer manufactured by IKA model RW 20 digital with the mixer speed kept at 230-330 RPM and the temperature of the water kept in the range of 29 – 31^{0}C by means of a thermal controller JULABO model ED and it was fixed on the feed water tank as shown in Figure 3.5

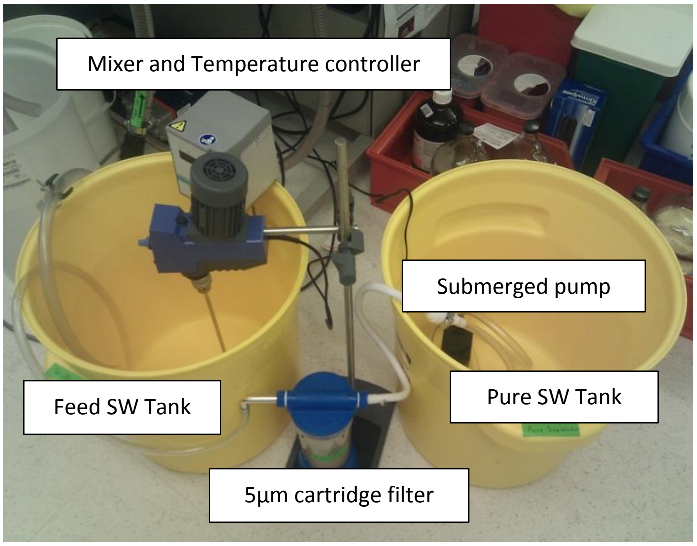

Figure III.5 Raw and Feed SW tanks

Then after heating the feed water to the required range to mimic the real sea water temperature in the summer, the experiment is ready to be run. The pumped water from the feed tank passes through a pressure gauge and flow meter prior to the membrane to control flow rate and applied pressure. The permeate is then collected in the product tank as shown in Figure III.4.

Each experiment was kept for 60 minutes run, then 2-2.5 minutes of backwashing in order to clean the membrane. Then permeability tested to assure the recovery of the membrane. The same pump was used for the backwash, so it has to be cleaned from the seawater residual in the pump head and the tubes before being used to backwash the membrane as shown in Figure III.4. About 15-20 liters of pure reverse osmosis (RO) water was used to clean up the sea water from the pump's head and tubes. Then the same RO water was used for backwashing. The backwash can be done by passing the RO water for about two minutes and with a flux rate of 300-350 lmh. However, longer backwashing time has been used in order to make sure that the membrane is perfectly cleaned. Manual backwash was done in two steps. The first one is the backwash to the bottom (BWB) side of the membrane at a flux rate 300 lmh for about 40 – 60 seconds. Then the processes continued by a backwash to the top (BWT) side of the membrane for another 40 to 60 seconds at a flux rate of 300lmh as well.

All experiments were conducted with the same procedure:

1- Permeation for 1 hour, either constant or variable flux depending on the experiment requirement.
2- Cleaning the pump and tubing with 15-20 L of RO water at a rate of 250 l/m^2xh and the pump speed 800 RPM.
3- Backwash at a rate of 200 l/m^2xh for 60 seconds on BWB mode then another 60 seconds in BWT mode.
4- Cleaning the feed SW tank and fill it with filtered SW and heat it to 29-31^{0}C
5- Repeat steps 1 to 4.

Experiments were done by varying the different operating parameters: pressure and permeate flux. Some experiments required addition of coagulant and it was added manually in the feed SW tank and after finishing the experiment the tank was cleaned and rinsed by RO water to make it ready for subsequent experiments.

Another valve was added on the other side of the membrane as shown in Figure III.4 that is used as an air valve which is opened at the beginning of each experiment in order to allow the air in the tubes to be released. The same valve is connected with a pressure gauge and tubes and that can deliver the water to the drain and/or to be recycled to the feed tank in case if the membrane module was used for cross-flow filtration mode (future investigation). Figure III.6 shows a photograph of the complete UF experimental unit.

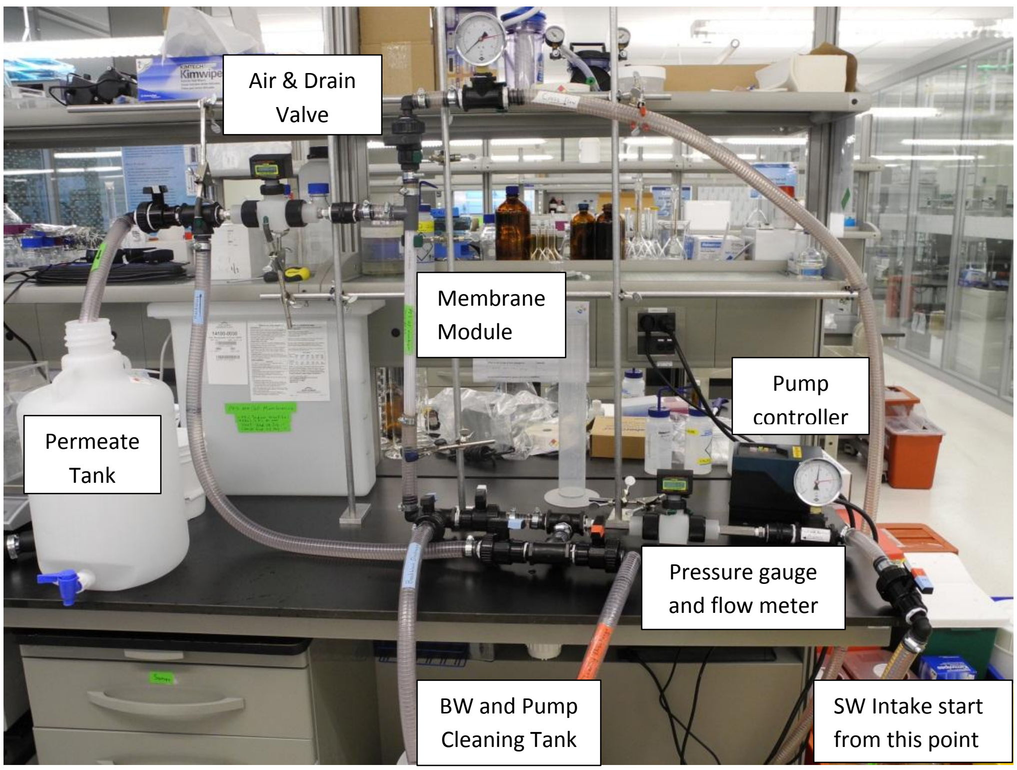

Figure III.6 Bench Scale membrane pretreatment System

3.4.2 Coagulation Method

Several factors affect the efficiency of the coagulation dose. Some of these factors are physical such as mixing method, mixing speed and intensity, as well as chemical factors such as pH, temperature and dose.

The two most commonly used conventional coagulants are Alum ($Al_2(SO_4)_3$) and ferric chloride ($FeCl_3$). While the former is better at lower pH, $FeCl_3$ has a better effect at higher pH. Other alternative coagulants such as PACLs (Poly Aluminum Chloride) and PFS (Poly Ferric Sulfate) are used but less practical [47]. For this research $FeCl_3$ have been used as coagulant for all experiments since the seawater pH is high (7.8 – 8.2). Beside that when comparing Alum with $FeCl_3$, studies found that Alum sticks more frequently on the membranes causing fouling problems [48].

Coagulation or destabilization of colloidal/dissolved matters depends on the amount of coagulant added. Inadequate dose will sufficiently destabilized and excessive doses can cause detrimental effect. Thus, there is an optimal dose at which coagulation is most effective. Adding coagulant beyond the optimum dose can have an adverse effect on the overall coagulation where a phenomenon called "restabilization" can occur [48]. This is illustrated in Figure 3.7

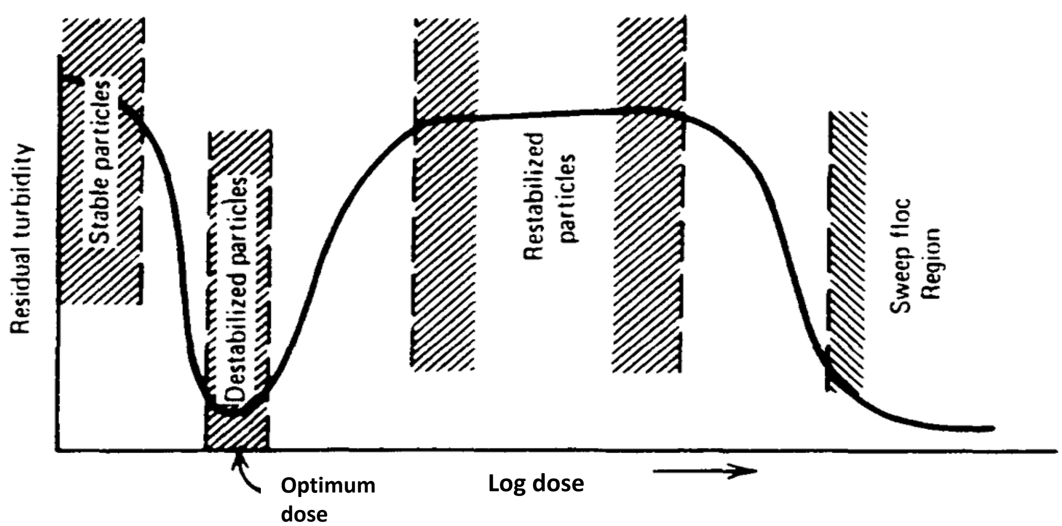

Figure III.7 Destabilization and restabilization in coagulation [47]

This figure also shows that low coagulation doses can cause ineffective coagulation but further addition of coagulant provide complete destabilization, where effective coagulation occurs due to charge neutralization mechanism. However, addition beyond this dose will result in restabalization because of near complete coverage of colloid/particulate with the hydrolysis product, which then repel each other [48]. Excess addition beyond this dose will cause coagulant to precipitate due to exceeding the solubility of the coagulant. These bulky precipitate can consume color and turbidity and remove them as they settle, this process is known as “sweep flocculation”. However, more coagulant would be demanded in this process which from economical point of view would be costly [47]. On the other hand, most of the water treatment plants coagulation process takes place in the sweep floc range because it is very difficult to coagulate the water by an optimum dose when the influent water quality is changing [49].

Ideally, the optimal coagulant concentration is determined by a jar test. However, this test has not been used in this study due to technical limitations. Alternatively, coagulation doses were arbitrarily chosen i.e. 1, 2, and 3 mg/L $FeCl_3$ concentrations have been used in order to optimize the dose.

In all experiments the coagulant has been added manually to the feed water by knowing the volume of the feed water in the feed tank. Then the process is done while the mixer was kept running continuously in order to make sure the maximum interactions between the feed water and the coagulant.

3.4.3 Filtration Experiments

The goal of this research is to determine the most proper membrane pretreatment configuration by testing three different membranes with different pore sizes: 0.1 MF, 100 kDa and 50 kDa.

As mentioned in Table III.1, different membranes with different coagulation concentrations have been tested in the experiments. Each test has been repeated eight times: four times with the 0.1 MF membranes with different coagulant concentrations (1.2 and 3 mg/l $FeCl_3$), three times with the 100 kDa with different concentrations of coagulant (1 and 2 mg/l $FeCl_3$) and one time with the 50 kDa membrane without coagulant addition.

The evaluation process has been divided into three main sections:

1- Constant flux, variable pressure vs. time
2- Constant pressure, variable flux vs. time

The aim of these two tests is to investigate the flux decrease at constant pressure and run the experiment under commercial operation mode, i.e. at constant flux and observe the pressure drop across the membrane in order to determine the frequency of membrane cleaning to control fouling. More details and analysis will be presented in chapter four.

3- Analyze the water parameters of the permeate after each run with different specifications in order to select the most appropriate economical procedure and water quality suitable for RO membranes.

3.5 Chemical Parameter Analysis Methods

This section will briefly describe the chemical water analysis parameters and the methods that have been applied on the samples.

3.5.1 Total Organic Carbon (TOC)

TOC are the amount of organic carbon present in water, both in dissolved and particulate phase while DOC is for the dissolved only. Analysis of TOC is imperative since it has immense impact on water treatment processes and applications. TOC was measured for raw water and permeate water samples using the equipment provided by Shimadzu called TOC-V CPH [50].

3.5.2 PH

pH was measured using CyberScan model pH 6000 Meter [51]. All samples were analysed in duplicate.

3.5.3 Conductivity and Total Dissolved Solids (TDS)

Both conductivity and total dissolved solids (TDS) of the raw and product water were measured using the equipment manufactured by OAKTON model CON 510 series Conductivity, TDS, ^{0}C /^{0}F meter [52]. All samples were analysed in duplicate.

3.5.4 Natural Organic Matter (NOM)

The LC-OCD (Liquid Chromatography - Organic Carbon Detection) manufactured by Siemens is the technique used to analyse natural organic matter (NOM) of different waters. It classifies NOM into about 10 classes of compounds and then detects them with customised organic carbon detector (OCD). All samples of raw water and permeates were analysed by the LC – OCD analyser in duplicates.

3.6 Physical Parameter Analysis Methods

This section will briefly describe the physical water analysis parameters and the methods that have been done on the samples.

3.6.1 Turbidity

Turbidity was measured with Hach 2100AN turbidimeter [53]. Turbidities of the raw and permeate waters were measured and recorded. All samples were analysed in duplicate.

3.6.2 Particle size distribution (Nano Sizer LM 20)

Intensity of particles in water sample also called particle size distribution (PSD) was measured for sea water and all permeate samples using the Nano Sizer LM20 machine manufactured by Malvern [54]. It is used to analyse the range of nano particles typically between 10nm – 1000nm depending on particle material. All samples were analysed in duplicate.

3.6.3 Silt Density Index (SDI)

The SDI test quantifies the content of particulate matter in water that plugs the membrane filter at a constant pressure and after certain time. The recommended SDI for RO feed is 3 (%/min) or less.

It consist of applying water at a constant pressure normally (30psi, 207kPa) to a membrane filter pore size of 0.45μm and then measuring the decrease in filter flow vs. time due to particulate material plugging the filter. Data collected to determine the filter plugging rate includes the initial rate of sample flow through a membrane filter, duration of filtration (5, 10 or 15 min) and a second or final flow rate through the filter. Then the following equation used to calculate the SDI value:

$$SDI_T = \frac{[\,1 - \frac{t_i}{t_f}]}{T}\ x\ 100$$

Where t_i is the initial time needed to fill 500ml container, t_f is the final time needed to collect final 500ml and T is the total time (5, 10 or 15min). The SDI value was measured for all samples and following the same procedure and most samples were analysed in duplicate.

3.6.4 Total Suspended Solids (TSS)

TSS was measured for raw water taken from the deep Red Sea water. TSS is reported in terms of mg of suspended solids/L of solution, it is quantified using a filtration method described as the total suspended solids dried at 103-105^0 C method. The experiment has been conducted according to the Standard method ESS Method 340.2: Total Suspended Solids, Mass Balance (Dried at 103-105 ^{0}C) [55].

3.8 Standard and Quality Control

One of the most important aspects of any analytical analysis is to ensure consistent results are obtained. This research focused on specific methods that aimed at quantifying a particular substance in water, and sometimes even comparing these results to those obtained earlier using the same method. Therefore, in order to ensure that the data obtained were statistically sound, a certain set of procedure was followed when sampling and/or analyzing water samples:

- Water quality parameters were always tested in duplicate, or in some cases in triplicate.
- Samples containers were always thoroughly cleaned and rinsed before collection of new sample to avoid any cross contamination and erroneous results.

Chapter IV

4.1 Results and Discussions

The following section describes the results obtained from the series of membrane tests performed during phase II of the research after the experiment set up phase. All experiments were conducted between June and July, 2011. 17 runs were performed. As previously mentioned, all experiments were performed using the bench-scale low pressure membrane system described in Chapter 3 of the thesis. During each run period, the feed pressure values, the feed and permeate flux rates and the permeate quality were collected and comparative results can be seen in this chapter highlighting how the different membrane pore size and coagulant concentrations affect the pre-treatment membrane system. In order to be able to make a comparative assessment for the treatment process, when comparing three different membranes the following objectives for this phase of the research has been set as follow:

- To examine the change in TMP while keeping the permeate flux constant over the time.
- To test the change in the permeate flux while keeping the pressure constant over the time.
- To investigate the effect of feed flow.
- To quantify the TOC and Turbidity removal, SDI, conductivity, NOM and other permeate quality parameters.

All of these objectives have been tested on the three membranes as follow:

- Examining and recording the performance of the three membranes without addition of coagulant ($FeCl_3$).
- Examining the 0.1 µm MF and 100 kDa UF membrane with the addition of 1 mg/l and 2 mg/l $FeCl_3$ coagulant.
- Examining the 0.1 µm MF membrane with the addition of 3 mg/l $FeCl_3$ coagulant.

4.1.1 Start-up phase

At the start of the experimental work, some runs have been done freely meaning without setting any specific parameters such as fixed pressure or fixed flux, on the 50 kDa UF membrane in order to understand the behaviour of the membrane and to get familiar with the tools and equipment and to have expectations about the results of the subsequent experiments.

Figure IV.1 representing the flux and pressure variation against time for the MF membrane. It shows a gradual pressure increase leading to 0.05 bar increment consistent with a gradual flux reduction for the first 30 min.

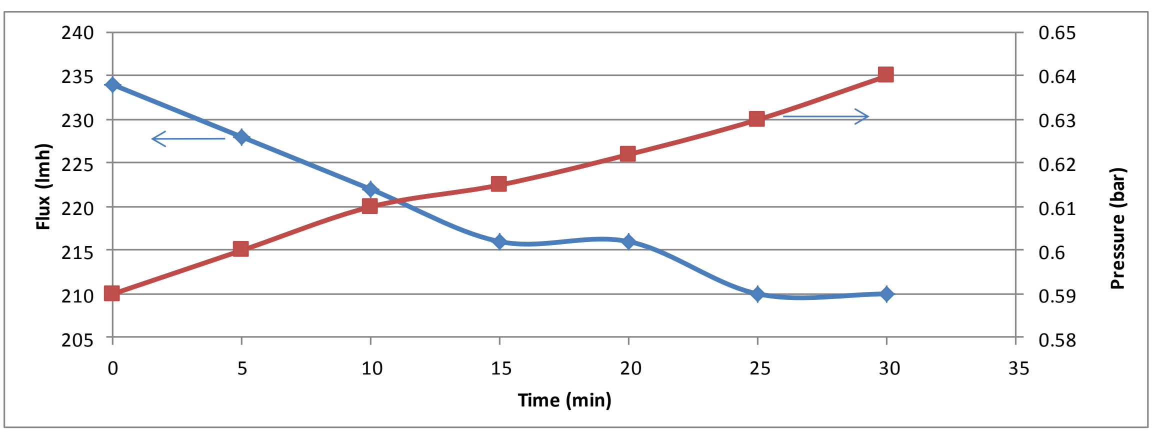

Figure IV.1 Increase in pressure and decrease in flux rate with time

Following the first experiment, several runs have been done on the membrane and with different backwash pressures and durations. The aim of the experiment was to get an overview and average values of backwash pressure and fluxes as well as the time required to clean the membrane. In subsequent experiments, the selected backwash operating parameters were used. Figure IV.2 shows the pressure increase with time and backwash frequency. While the sea water was used for the feed and RO water for the backwash to clean the membrane, it is noticeable that after each backwash the permeability of the membrane is not fully recovered meaning that there is some portion of the fouling that is known as irreversible fouling fraction. This required a chemical enhanced backwash after certain times of runs.

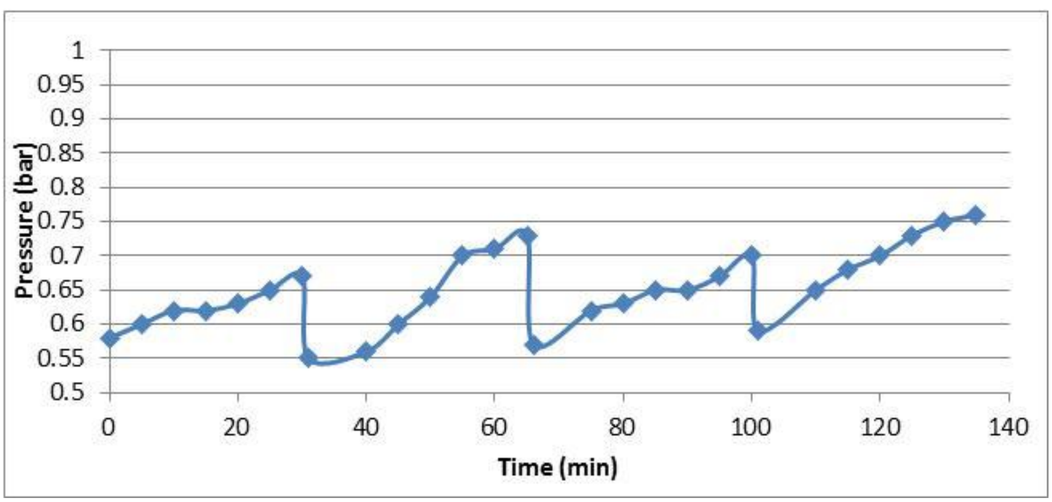

Figure IV.2 pressure changes over the time with both feed and backwash

In addition to that, even-though the cross flow configuration has not been covered in this research, a test for the membrane in cross-flow mode has been done. Two runs have been done at constant pressure mode and the brine was re-circulated in the feed tank. At a permeate flux of 95lmh the applied pressure was increased by 0.01 bar in 5 minutes.

Similarly, another experiment was performed by rejecting the brine and keeping the applied pressure constant at 1.0 bar. It was found that the permeate flux decreases and reached a steady state. It is interesting to investigate cross flow mode in terms of flux stability, cleaning frequency and economics in future work.

4.2 Constant Flux Experiments

Figure IV.3 to 4.5 show the experiments that have been done at constant flux mode. The flux has been kept at J=240lmh and as expected, the applied pressure increased due to the blockage of the membranes pores and/or cake layer formation. The main objective in this part is to investigate the influence of particle size and distribution for different membrane pore sizes with and without coagulation on the pressure increase in dead end filtration mode. Of course, the configuration that yields to more stable pressure and a lesser amount of increase in pressure is more preferable.

All the experiments were conducted in the same manner. The feed water temperature was kept at 30^0C (summer season seawater temperature) and only dead end mode with constant flux was examined. Data for pressure variation with time was collected every five minutes. Permeate flux was also measured continuously to make sure that it is kept constant. The permeate flux was controlled by changing the feed flux by means of the pump controller. Membranes were backwashed every one hour of filtration. Runs have been carried out twice and some experiments were carried out three times to get more accurate readings.

Figure IV.3 shows the relative pressure with time of the 0.1 MF membranes for different coagulation concentrations. Generally, there is gradual increase in the pressure with time with all the different coagulant doses. However, the pressure escalation slows down and behaves more steadily with the increase of coagulant concentration meaning that addition of coagulants enhanced the performance of the membrane. On the other hand, when comparing between the 1, 2 and 3 mg/l Table IV.1

Table IV.1 Relative Pressure diffrence over the time for 0.1um MF membrane at constant flux

$[FeCl_3]$, mg/l	Δ Pi/P0, %
0	54.8
1	8.0
2	20.0
3	10.7

It is observed that the 1mg/l $FeCl_3$ coagulant concentration gives the least increase in pressure with time which makes it the most preferable configuration for the 0.1 MF membrane. The relative pressure in this configuration shows the minimum growth making a relative pressure difference of 8.0% at the end of the filtration period (60 min).

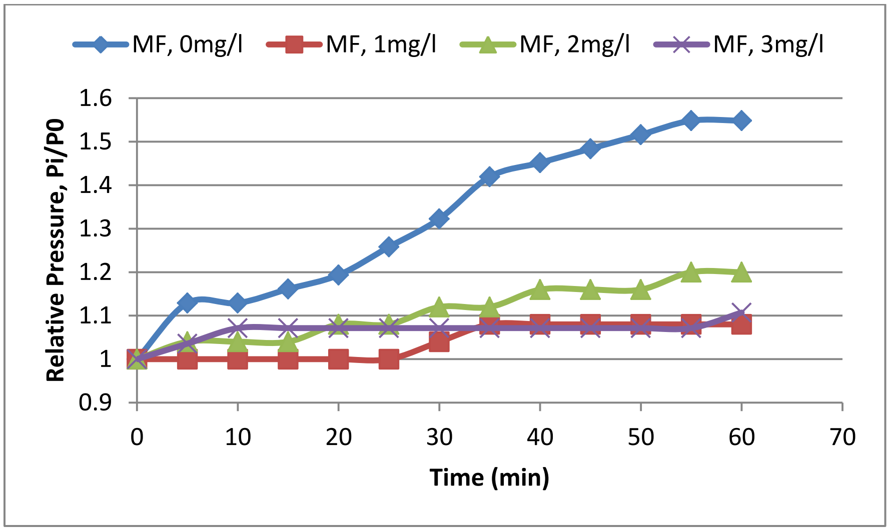

Figure IV.3 Pressure trends for different coagulant doses on 0.1MF membrane at constant flux filtration

On the other hand, Figure IV.4 presents the results of runs conducted on the 100kDa UF membrane with different coagulant concentrations. Almost the same as the previous implication, the pressure turns out to be more stable as the concentration of the coagulant increases. However, by looking at the relative pressure performance of each configuration with time Table IV.2

Table IV.2 Relative pressure trends for different coagulant doses on 100kDa UF membrane at constant flux filtration

[$FeCl_3$], mg/l	Δ Pi/P0, %
0	47.2
1	22.22
2	12.22

It shows that experimentally the 2mg/l with the lowest Δ Pi/P0 % is the most preferable option. But by looking again to the plots in figure 4.4 it shows that after 50min operation, a sudden increase in the pressure happened for the 1mg/l and this can be due to an operational mistake since the feed water in the tank reaches its low level which causes the pump to push the settled suspended solids with water and this causes this rapid pressure increase at the end.

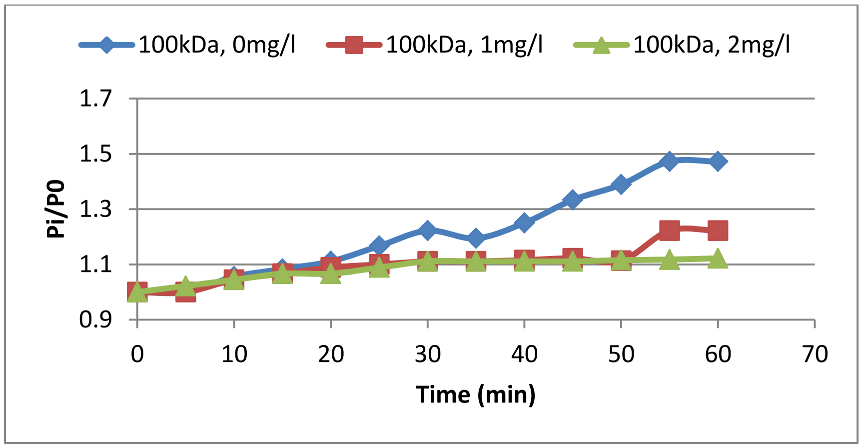

Figure IV.4 Pressure trends for different coagulant doses on 100 kDa membrane at constant flux filtration

So, by eliminating the last 10min of the run and redraw the graphs as shown in Figure IV.5

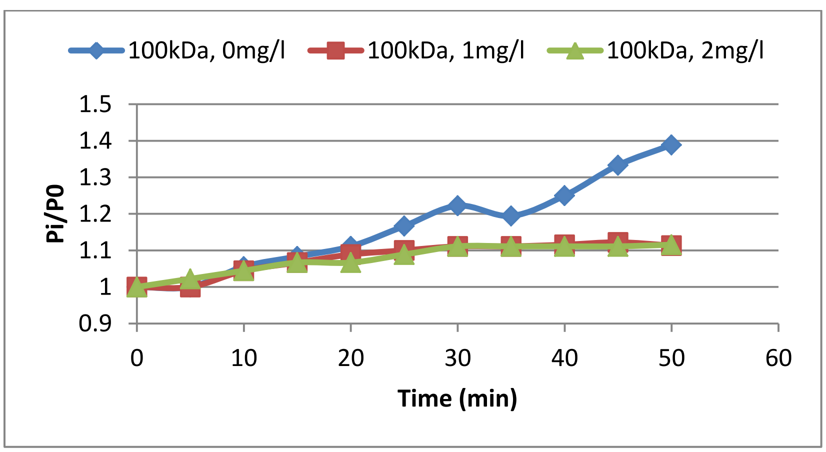

Figure IV.5 Pressure trends for different coagulant doses on 100 kDa membrane at constant flux filtration with the first 50min running time

It is clear that the performance of 1mg/l and 2mg/l is almost the same in terms Δ Pi/P0 % in Table IV.3 which indicates that the 1mg/l is enough for the membrane to do its best performance and a less chemical used, hence it is the optimum option for this case.

Table IV.3 Pressure trends for different coagulant doses on 100kDa UF membrane at constant flux filtration for the first 50min runing period

$[FeCl_3]$, mg/l	Δ Pi/P0, %
0	38.89
1	11.33
2	11.56

The last run presented in Figure IV.6 shows the 50 kDa membrane experiment and in this case higher relative pressure was explored Δ Pi/P0 = 19.2 % throughout the whole experiment duration. In this case, the 50kDa is considered as a less preferable option to be used for SWRO pre-treatment.

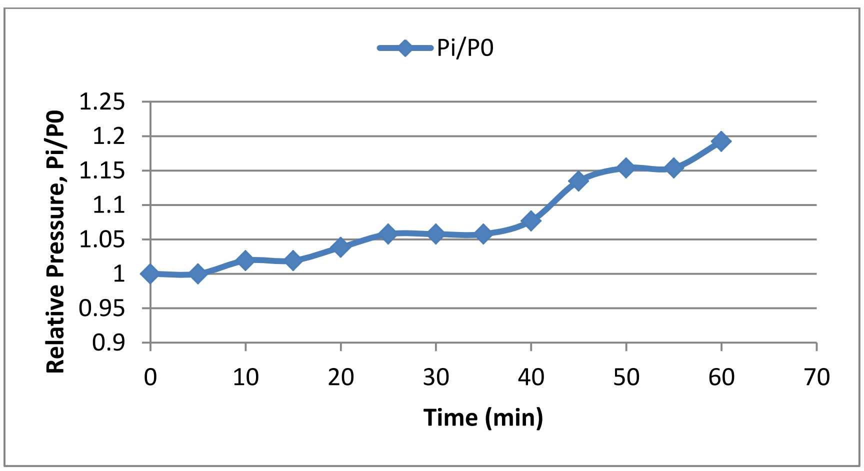

Figure IV.6 Pressure trends without coagulant doses on 50 kDa membrane at constant flux filtration

The comparison between the optimum cases in the three membranes is shown in the following Table IV.4.

Table IV.4 The minimum pressure difference between the first and last pressure reading for the optimum configurations on the three membranes in constant flux mode.

Membrane	Configuration	Δ Pi/P0, %
0.1 MF	1 mg/l $FeCl_3$	8.0
100 kDa	1 mg/l $FeCl_3$	11.3
50 kDa	No Coagulant	19.2

By looking at the results presented in Table IV.4, it can be concluded that 0.1 MF membranes with the 1 mg/l $FeCl_3$ represents the most suitable and preferred membrane pretreatment system scheme when taking the constant permeate flux as the optimum objective. Then, followed by the 100kDa membranes with 1mg/l coagulant injection as a second recommended option. However, as it will be shown later on this chapter all membranes performed well and provided RO feed water of very high quality.

4.3 Constant Pressure Experiments

In this section another series of experiments have been done but with different objectives. The aim of this part is to examine the decrease in the permeate flux while keeping the pressure constant. The applied pressure was kept constant by adjusting the pump RPM speed and the pressure valve even when the membrane fouling occurs. By looking at the Figure IV.7 to 4.8, data of permeates fluxes versus time were collected every five minutes and the pressure was kept at, P_0 = 0.4bar for all the runs. As expected, there is a decrease in permeate flux with time. However, this decrease varies with different membranes used and coagulant concentration. The goal of this part is to find out the configuration that leads to the minimum possible decrease in flux.

By looking at the plots of Figure IV.7, the following results on the 0.1μm MF membrane can be summarised: It is observed that the first run that is done without using any coagulant cannot be successful since it has the highest relative flux, J_0/J_i drop. The flux decreases dramatically within 60 minutes running duration and this represents 52% decline as shown in the relative flux rate in Figure IV.7. However, as the concentration of the coagulant increases from 1mg/l to 3 mg/l of $FeCl_3$ the stability of the flux rate enhanced and the difference in relative flux decreased (Table IV.5).

Table IV.5 Difference in relative fluxes with time for 0.1um MF membrane at different coagulant concentrations, at constant P experiment.

$[FeCl_3]$, mg/l	Δ Ji/J0, %
0	47.6
1	28.6
2	23.6
3	4.8

Theoretically speaking the flux Δ Ji/J_0 = 4.8% with the 3mg/l is the most preferable option in this case, however, from economic and environmental point of view, using less coagulant is preferred , if possible, and by looking at Table IV.5 it is noticeable that the 1 and 2 mg/l $FeCl_3$ almost have the same relative pressure drop. So, by comparing higher coagulant use with lesser Δ Ji/J0 drop with one third of the coagulant used with a higher Δ Ji/J0 increase but still in the acceptable range, it is concluded that the 1mg/l $FeCl_3$ is preferable option. In this case it is more suitable to choose the 1mg/l since it involves less chemical use and less cost.

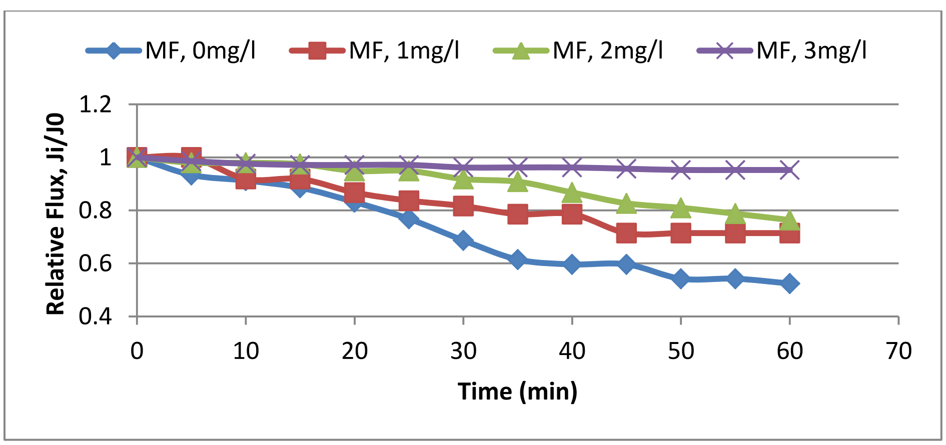

Figure IV.7 Flux behaviors at different coagulant doses on 0.1um MF membrane at constant pressure filtration mode

On Figure IV.8 the runs done with the 100 kDa membrane are shown. In these three runs, the first one without using coagulant represents the worst case. On the other hand, the second and the third that have a coagulant concentration of 1mg/l and 2mg/l respectively, have almost the same behaviour. By comparing the relative fluxes loss over the 60 minutes running time for both of them, it indicates that the flux with 1mg/l coagulant concentration has decreased by 18% and the same conclusion was given for the 2mg/l run as well.

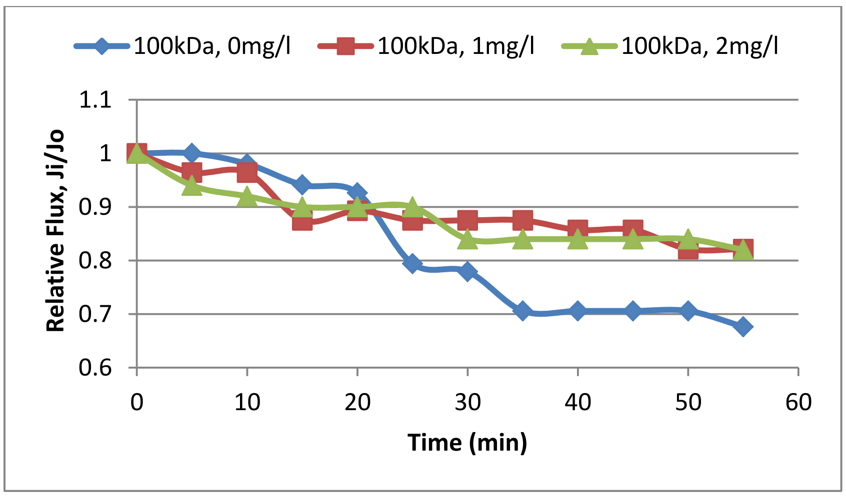

Figure IV.8 Relative flux behaviors at different coagulant doses on 100kDa UF membrane at constant pressure filtration mode

As a conclusion for this point, it can be said that there is no noticeable change in the relative flux rate loss between the 1mg/l and 2 mg/l coagulant concentration in the long term operation and hence it is recommended to use the less coagulant concentration that is the 1mg/l $FeCl_3$ concentration.

The last Figure IV.9 of this series of experiments represents the run that has been done on the 50 kDa membrane without using coagulant. By looking at the plot, the relative flux dropped down to 0.83 and by taking the difference, there is a loss equivalent to 16.7% in flux rate. In this case, this ratio is better than the other three proportions taken in the 100 kDa case.

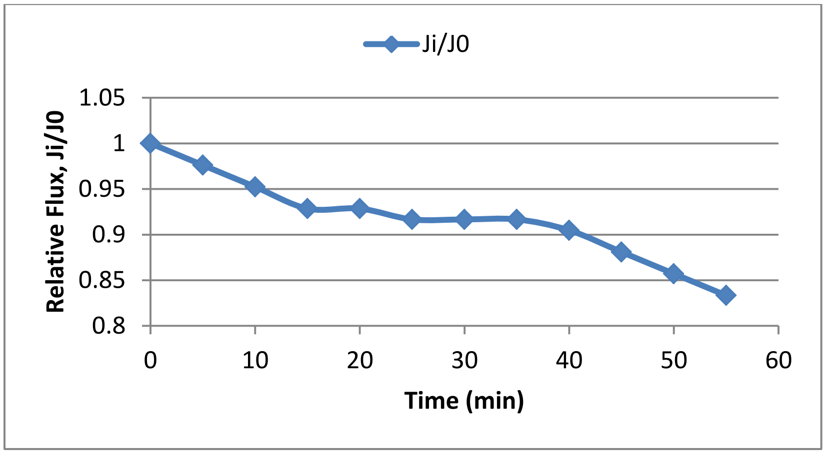

Figure IV.9 Flux behaviors without coagulant dosing on 50kDa UF membrane at constant pressure filtration mode

As a conclusion for all the previous three steps, the following Table IV.6 presents the optimum case of each of them

Table IV.6 Loss in relative fluxes for the best three configurations in the constant pressure phase

Membrane	**Configuration**	**Δ Ji/J0, %**
0.1 MF	1 mg/l $FeCl_3$	23.0
100 kDa	1 mg/l $FeCl_3$	18
50 kDa	No Coagulant	16.7

By comparing the results shown in Table IV.6, it can be seen that the most preferable configuration is the 50 kDa membrane without coagulant followed by the 100 kDa membranes with 1 mg/l $FeCl_3$ and then the 0.1 µm MF with 1 mg/l $FeCl_3$ coagulant concentration because it has the highest Δ Ji/J_0 % reduction. However, it is important to notice that the three Δ Ji/J_0 % reductions are close to each other and by looking to another factor which is the initial flux of each configuration as shown in Figure IV.10. It is observed that the 0.1 MF with 1mg/l has the highest flux and also it produces around double the permeate volume which is produced by the 50kDa. So, as a final conclusion from economical point of view the 0.1 MF with 1 mg/l is the most preferable option then the 100kDa UF with 1mg/l and the least preferred is the 50kDa UF without coagulation.

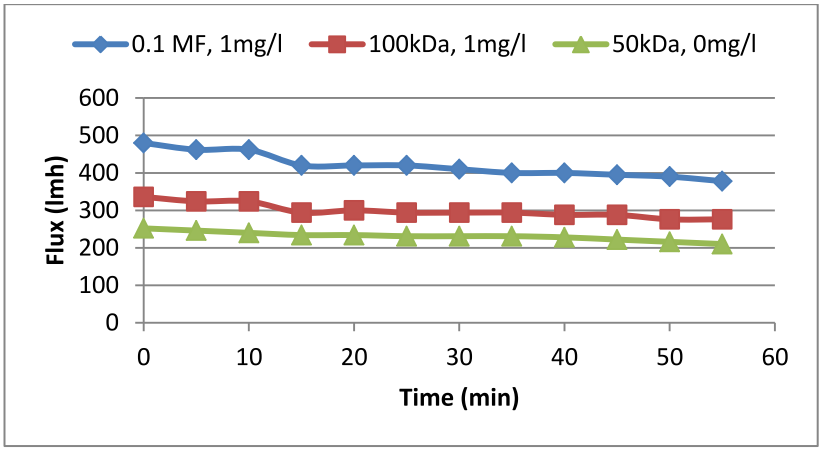

Figure IV.10 Initial flux for the three best configurations

4.4 Permeate Water Quality Parameters and Analysis

The quality of permeate is the most important factor in the whole experiment since it has to be within the acceptable range that is required for the RO membranes that is supposed to receive this permeate. All permeates produced by the different membranes have been analysed and the following Table IV.7 summarises the water parameters that have been measured:

Table IV.7 Water Parameters Analysis

	seawater	50 kDa w/o coag.	100 kDa w/o coag.	100 kDa + 1mg/l	100 kDa + 2mg/l	0.1 MF w/o coag.	0.1 MF + 1mg/l	0.1 MF +2 mg/l	0.1 MF + 3mg/l
SDI (%/min)	11.91	2.70	2.88	1.81	1.2	1.89	2.77	2.49	1.67
Turbidity (NTU)	0.60-0.75	0.06	0.14	0.06	0.06	0.17	0.18	0.10	0.13
PH	8.36	7.82	7.56	7.15	7.25	7.79	7.23	7.19	7.57
Conductivity (mS)	60.5	60.6	55.2	57.3	56.7	60.9	58.6	59.6	57
TDS (ppt)	30.1	30.4	27.6	28.6	28.3	30.4	29.1	29.9	28.5
TOC, (mg/l)	1.94	1.652	1.82	1.76	1.05	1.665	1.481	1.62	1.06
Nano-Sizer	attached	attached	Attached	attached	attached	attached	attached	attached	attached
Temperature (^{0}C)	20.2	20.4	22.6	21.3	21.3	24	24.5	25.5	22.5

4.4.1 Assessment of Water Parameters Analysis

As clearly seen Table IV.7, some parameters have changed dramatically after passing through the membranes such as SDI_{15} and turbidity, while some other parameters have been slightly improved. The following points will summarize the most important changing parameters:

1- In general, the recommended value for SDI_{15} to be below 3 for all permeate samples and it was achieved. However, results comparison between the best cases among the three membranes, presented in Table IV.8, show that the 100kDa membrane with 2mg/l coagulant concentration injected in the feed seawater has a better value than the two other membranes.

Table IV.8 SDI values for different membranes

	0.1 MF + 3mg/l	100 kDa + 2mg/l	50 kDa w/o coag.
SDI_{15}	1.67	1.20	2.70

In contrary, the 0.1μm MF membrane with addition of 3mg/l coagulation in the feed can give a value even less that 2, which means it is still highly recommended to be used in the pretreatment stage for any RO system. The 50kDa membrane resulted permeate with SDI_{15} = 2.7, which is closer to the RO membranes recommended value than the previous two samples. It can be concluded from the last result that the use of $FeCl_3$ as a coagulant has a positive impact on the permeate quality.

2- Turbidity reductions were also consistent in all experiments that have been done with all the membranes. Table IV.7 above shows that the highest removal rates were 85 – 92 % with the smallest pore size membrane, 50kDa, and with the 100kDa membrane with coagulation. The lowest turbidity removal achieved when using the 0.1MF membrane was 75 - 85 % which is still considered good but not as much as the previous cases.

These results were also expected, as the UF membrane was designed to exclude turbidity in the form of particulate matter, which is much larger in size than the NOM. Despite the water turbidity was varying between 0.6-0.7NTU, the permeate turbidity was found very low and constant. This result was expected as UF membranes act as total barriers for particles.

3- As expected, it is observed that there were very little TDS and TOC removals through the membranes due to the membrane pore size. The smallest nominal MWCO of the membranes is 50kDa. So, it can be concluded that in order to achieve better removal, smaller pore sizes of the membrane should be used. Another notice that can be seen in the table is that greeter TOC removal has been achieved when using greater $FeCl_3$ dosage; i.e. 2mg/l for 100kDa and 3mg/l for 0.1 MF membrane. The details of the natural organic matter fraction removal given by the analysis done by the LC- OCD are given on the following point.

4- As shown in Table IV.9 since the bio-polymers (BP) has the largest size, there is a significant percentage removal of BP and this percentage increases with smaller membranes pore sizes. Also, results show that in general there is a better BP removal when using the coagulant. However, in case of MF, 3mg/l and 100kDa UF, 2mg/l, results shows that the concentration of BP has started to increase which means those concentrations are overdosed. On the other hand, the table does not show a significant removal of the other three fractions which are Humic substances, Building block and Neutrals and this is because of the their sizes which are so smaller than the MF and UF membranes to be removed even with the help of coagulants.

Table IV.9 LC-OCD results for NOM fraction remoal

	approximate molecular weights (g/mol):			
	>>20.000	*~1000*	*300-500*	*<350*
Sample	Bio-polymers	Humic Subst. (HS)	Building Blocks	Neutrals
Sea water	267	635	265	742
MF, 0mg/l	177	581	265	744
MF, 1mg/l	145	618	347	731
MF, 2mg/l	135	563	262	666
MF, 3mg/l	137	559	260	749
100kDa UF, 0mg/l	131	549	236	746
100kDa UF, 1mg/l	112	537	226	726
100kDa UF, 2mg/l	153	576	248	706
50kDa UF, 0mg/l	126	525	237	718

5- Particle size analysis given by Figure 4.11 shows that all the configurations performed as expected in terms of particle removal relative to the sea water particle content. 50kDa achieved the best particle removal by having a fraction of smallest particle size. All variations in 0.1µm MF and 100 kDa UF also removed significant portion of particle. However, the deviant fraction found in the case of 100kDa UF might be resulted by contamination of the water sample.

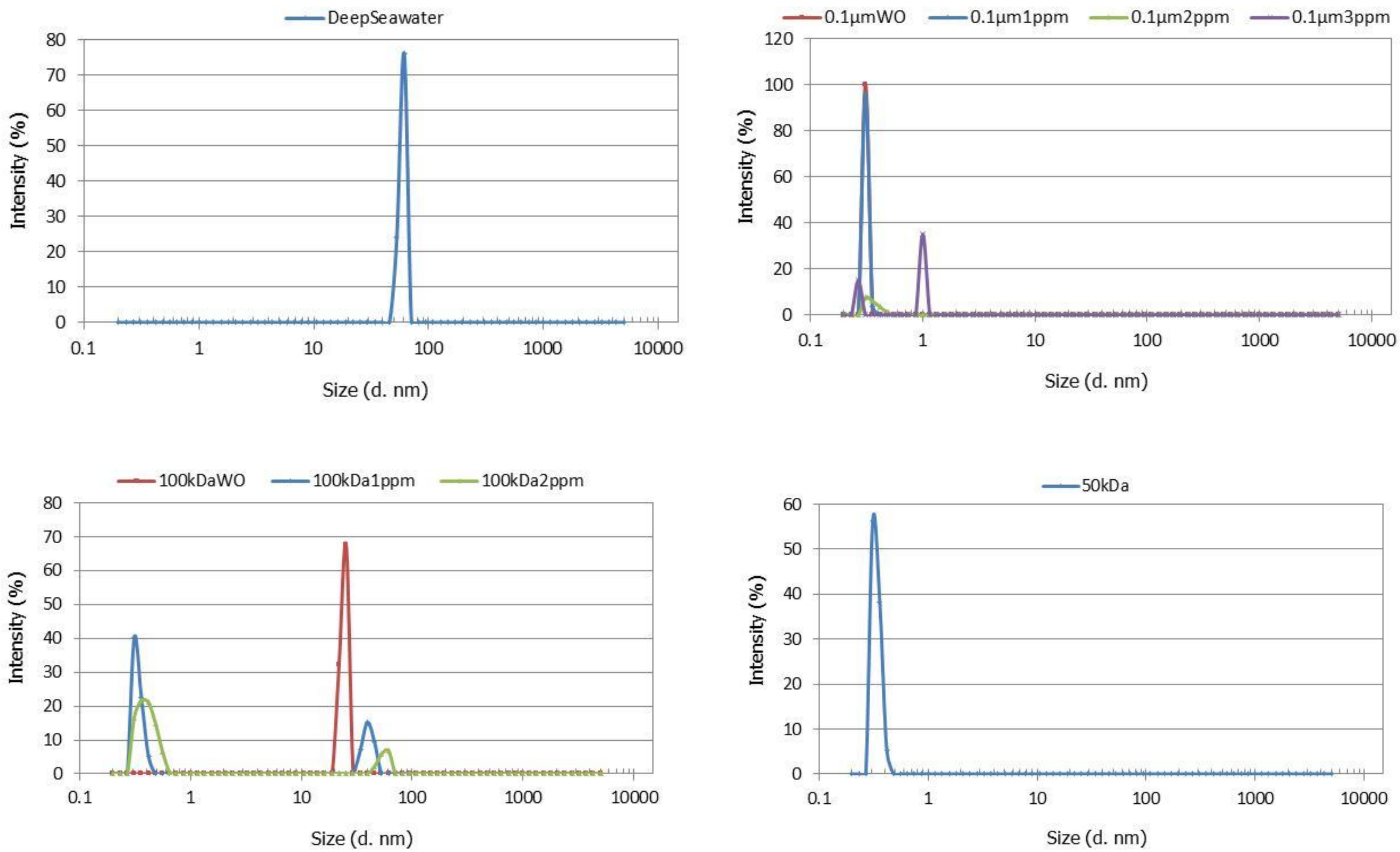

Figure IV.11 Particle size distribution (PSD)

Chapter V

5.1 Conclusions

The following conclusions are primarily focused on the response and behaviour of the three low pressure membranes used with different configurations. Two main experiments have been tested and analysed. The first one was performed at constant pressure and the second one at constant flux. The permeate flux and pressure variations were then investigated, respectively. The water quality after each experiment was analysed. Eight different runs have been done on each experiment as follow:

- 0.1µm MF membrane combined with (0 mg/l, 1 mg/l, 2 mg/l and 3 mg/l) $FeCl_3$ coagulant concentration in the feed sea water.
- 100kDa UF membrane combined with (0 mg/l, 1 mg/l and 2 mg/l) $FeCl_3$ coagulant concentration in the feed sea water.
- 50kDa UF membrane without the addition of coagulant.

Based on the work presented in this thesis, the following conclusions can be made

1- For Constant Flux Operation:

a- It is concluded that 0.1 MF membranes with the injection of 1 mg/l $FeCl_3$ represents the most suitable and preferred membrane pretreatment scheme with an increase of 8.0% relative pressure after 60 minutes filtration.

b- The second preferred configuration is the 100kDa UF membrane with 1 mg/l $FeCl_3$ injection. The relative pressure has increased in this test by 11.33% after 1 hour filtration. Finally, the third preferred option is the 50kDa UF membrane without addition of coagulant but the pressure of this run increased by 19% by the end of the filtration period.

2- For Constant Pressure Operation:

a- The results of this experiment showed that the 0.1 µm MF membrane with 1 mg/l $FeCl_3$ coagulant concentration in the feed is the most preferable because the permeate relative flux has lost 23.6% from its initial rate after 60 minutes.

b- The loss in relative permeate flux in the 50kDa configuration was 16.7%. The 100kDa UF membrane with coagulant concentration of 1 mg/l $FeCl_3$ has lost 18% of its original relative flux which is still good but not better than 0.1µm case or the 50kDa UF.

3- Water quality analysis after each trail concluded the following shared results:

a- All the experiments are capable of producing permeate with SDI_{15} less than 3, but the most preferred configurations are the 100kDa and 0.1 µm MF membranes with 2 and 3 mg/l FeCl3 coagulant concentrations, respectively. Permeate of the 50kDa membrane without coagulation has an SDI_{15} value of 2.7 which is less than 3 and hence it is also affordable and can be used as a pretreatment for the RO membranes.

b- The turbidity was very well removed by all the membranes, with the permeate stream having a value below 0.15 NTU on average. The highest turbidity removal was achieved consistently with the smallest pore size membranes, namely, the 50kDa UF membrane then the 100kDa with 1 and 2 mg/l $FeCl_3$ coagulant concentrations. Turbidity removal of 85 – 92 % was achieved by the previous two membranes while this percentage is reduced to 75 – 85 % removal when using the 0.1 µm MF membrane with different coagulant concentrations.

From this, it can be concluded that MF and UF membranes provided high quality RO feed water with/without using coagulant. However, the 0.1 µm MF membrane with 1mg/l $FeCl_3$ has achieved the optimum case in this research and it is advised to be used for SWRO pretreatment. The second most preferable choice is the 100kDa UF membrane with 1mg/l $FeCl_3$. While the last preferred option, but is still very efficient, is the 50 kDa UF membrane without coagulant dosing. However, keeping in mind that not using a coagulant may not be a safe option to control membrane fouling and permeate water quality as raw water susceptible to change in TSS concentration and distribution. In addition, low coagulant dosing could act as a safe option to control the process.

5.2 Recommendations

The following recommendations should be considered for future work.

1- Considering the same experiment set up, the following is a list of recommendations that can be conducted to enhance and support the results presented in this research.

   a- Only dead end filtration mode was examined in this research. A further study can be achieved with a cross-flow filtration mode. As mentioned before, the cross-flow filtration has an advantage of less backwashing requirement and hence further studies can be achieved on the behaviour of the different membranes. However, energy consumption will be higher as the required feed flux is much higher.

b- Different coagulants can be used and then comparison between different coagulants can be done based on improvement of the water quality and the decrease of the membrane fouling.

c- In this experiment no chemical enhance backwash (CEB) was performed. In the future CEB can be applied to evaluate the performance of the membranes and cleaning frequency for longer operation.

d- Another way to expand on this research is to conduct the experiments during different seasons where temperature changes and other conditions such as raw water quality changes can affect the process and fouling /biofouling control which eventually affect the membrane efficiency.

e- The experiment should test different flux rates in order to reach the optimum flux rate that leads to the minimum fouling [7]

f- Coagulant dose should be added at an automated continuous mode on on-line bases while the feed is being pumped to the membrane. In this study coagulation was done manually which may not be effective for organic matters removal. However, the advantages of the automated method is to guarantee removing the particles/ colloid matter as well as large portion of natural organic matters NOM that have smaller particles sizes.

2- Future experiments should include different types of membrane materials, because all the membranes that were used in this project are made from PES material. Also, further research can be done on more different membranes' pore sizes and configurations (out – in) mode.

3- Recommendations that can be done to improve the existing experiment set up:

a- Further experiments should be conducted on the membranes after fouling in order to better understand which type of materials are responsible for membrane fouling. So that further research can be done to improve the membrane materials and also in the chemical used for backwashing.

b- This experiment set up was designed to be operated manually. However, in order to decrease the errors, the whole system should be automated.

REFERENCES

1. Development, U.M., *World Summit on Sustainable Development, Plan of Implementation* 2002.

2. Samir S. Amr, A.T., *Jabir ibn Hayyan.* Ann Saudi Med, 2007. **27**(1): p. 53-54.

3. Khawaji, A.D., I.K. Kutubkhanah, and J.-M. Wie, *Advances in seawater desalination technologies.* Desalination, 2008. **221**(1-3): p. 47-69.

4. Bushnak, A.A., *Desalination* in *Arab Environment: water*2010. p. 125 - 136.

5. Cooley, H., P.H. Gleick, and G. Wolff, *Desalination, with a grain of salt.* Pacific Institute. June, 2006.

6. *Desalination Yearbook, IDA* 2010-2011: Water Desalination Report.

7. A Brehant, V.B., M Perez, *Comparison of MF/UF pretreatment with conventional filtration prior to RO membranes for surface seawater desalination.* Desalination 2002. **144**(1-3): p. 353-360.

8. *The 6th Saudi Water & Power forum Session ,Summaries and Outcomes.* in *Saudi Water and Power Forum (SWPF 2010)*. 2010. Jeddah, Saudi Arabia: Al-Aghar Group.

9. *Tsiourtis*, N.X., *Desalination and the environment.* Desalination, 2001. **141**(3): p. 223-236.

10. *Pankratz*, T., *Desalination technology trends*, 2005, CH2M Hill Inc.

11. Kabsch-Korbutowicz, M., A. Bilyk, and M. Molczan, *The Effect of Feed Water Pretreatment on Ultrafltration Membrane Performance.* Polish Journal of Environmental Studies, 2006. **15**(5): p. 719-725.

12. AG, S. *How does Microfiltration compare with Conventional Pretreatment Systems?* Water and *Wastewater* Library 2011; Available from:

http://www.water.siemens.com/en/applications/water_and_wastewater_library/Pages/industrial_reuse_mf_compared_conventional.aspx.

13. Lorain, O., et al., *Ultrafiltration membrane pre-treatment benefits for reverse osmosis process in seawater desalting. Quantification in terms of capital investment cost and operating cost reduction.* Desalination, 2007. **203**(1-3): p. 277-285.

14. Nicolaisen*, B., Developments in membrane technology for water treatment. Desalinati*on, 2003. **153**(1-3): p. 355-360.

15. Pearce, G., *SWRO pre-treatment: Markets and experience.* Filtration & Separation. **47**(4): p. 30-33.

16. Prihasto, N., Q.-F. Liu, and S.-H. Kim, *Pre-treatment strategies for seawater desalination by reverse osmosis system.* Desalination, 2009. **249**(1): p. 308-316.

17. Drioli, E., et al., *Integrating Membrane Contactors Technology and Pressure-Driven* Membrane *Operations for Seawater Desalination: Energy, Exergy and Costs Analysis.* Chemical Engineering Research and Design, 2006. **84**(3): p. 209-220.

18. N. KUBOTA, T.H., and Y. MORI, *Microfiltration and Ultrafiltration*, in *Advanced Membrane* Technology *and Applications*, A.G.F. Norman N. Li, W. S. Winston Ho, and T. Matsuura, Editor 2008, John Wiley & Sons, Inc.: Fuji City. p. 101 - 129.

19. D. KENNEDY, J.K., S. G. SALINAS RODRI ´GUEZ, N. H. LEE, J. C. SCHIPPERS, and G. AMY, *Water Treatment by Microfiltration and Ultrafiltration*, in *Advanced Membrane* Technology *and Applications*, A.G.F. Norman N. Li, W. S. Winston Ho, and T. Matsuura, Editor 2008, John Wiley & Sons, Inc: 2601 DA Delft. p. 131 - 170.

20. Mulder, M., *Basic principles of membrane technology*1996: Springer.

21. *Chapter 12 Future trends of inorganic membranes and membrane reactors*, in *Membrane* Science *and Technology*, H.P. Hsieh, Editor 1996, Elsevier. p. 569-582.

22. *Chapter 1 Overview membrane technology*, in *Membrane Science and Technology*, C.J.M.v. Rijn, Editor 2004, Elsevier. p. 1-23.

23. Brown, L.R. and W. Institute, *State of the World.* 1984.

24. Advanced Nanofabrication, I.a.C.C.L., 2011, King Abdullah University of Science and technology KAUST: Thuwal 23955-6900, KSA.

25. Côté, P., et al., *A new immersed membrane for pretreatment to reverse osmosis.* Desalination, 2001. **139**(1-3): p. 229-236.

26. Alspach, B., *Microfiltration and ultrafiltration membranes for drinking water.* American Water Works Association, 2008. **100**(12): p. 84-97.

27. Chen, V., *Performance of partially permeable microfiltration membranes under low fouling conditions.* Journal of Membrane Science, 1998. **147**(2): p. 265-278.

28. Walsh, M. and G. Gagnon, *Evaluating Membrane Processes for Drinking Water Treatment Design.*

29. Fane, A.G., C.J.D. Fell, and A.G. Waters, *The relationship between membrane surface pore* characteristics *and flux for ultrafiltration membranes.* Journal of Membrane Science, 1981. **9**(3): p. 245-262.

30. Huisman, I.H., et al., *Water permeability in ultrafiltration and microfiltration: Viscous and electroviscous effects.* Desalination, 1997. **113**(1): p. 95-103.

31. Tarnawski, V.R. and P. Jelen, *Estimation of compaction and fouling effects during* membrane *processing of cottage cheese whey.* Journal of Food Engineering, 1986. **5**(1): p. 75-90.

32. B.V, L. *http://www.lenntech.com/ultrafiltration/ultrafiltration-membrane-configuration.htm*. 1998-2011 [cited 2011 7/14/2011].

33. Group, K.C.T. *KOCH membrane systems*. 2004-2011 2011; Available from: http://www.kochmembrane.com/prod_hf.html.

34. BV, X.-F., *Seawater Pre-treatment*, D.E. 5, Editor 2009, Norit Corporate: Enschede.

35. Hillis, P., et al., *Effects of backwash conditions on out-to-in membrane microfiltration.* Desalination, 1998. **118**(1-3): p. 197-204.

36. Michael Pilutti, P., Julia E. Nemeth, PE,, *TECHNICAL AND COST REVIEW OF COMMERCIALLY AVAILABLE MF/UF MEMBRANE PRODUCTS.* International Desalination Association. **BAH03-029**.

37. van Hoof, S.C.J.M., J.G. Minnery, and B. Mack, *Dead-end ultrafiltration as alternative pre-treatment to reverse osmosis in seawater desalination: a case study.* Desalination, 2001. **139**(1-3): p. 161-168.

38. Watertechnologies, I., *Ultrafiltration Technichal Manual*, 2010, Inge: Greifenberg, Germany.

39. Cho, J., G. Amy, and J. Pellegrino, *Membrane filtration of natural organic matter: factors and mechanisms affecting rejection and flux decline with charged ultrafiltration (UF) membrane.* Journal of Membrane Science, 2000. **164**(1-2): p. 89-110.

40. Lee, N., et al., *Identification and understanding of fouling in low-pressure membrane (MF/UF) filtration by natural organic matter (NOM).* Water Research, 2004. **38**(20): p. 4511-4523.

41. Al-Sheikh, A.H.H., *Seawater reverse osmosis pretreatment with an emphasis on the Jeddah Plant operation experience* 1.* Desalination, 1997. **110**(1-2): p. 183-192.

42. Ebrahim, S., et al., *Fifteen years of R&D program in seawater desalination at KISR Part I. Pretreatment technologies for RO systems.* Desalination, 2001. **135**(1-3): p. 141-153.

43. Bonnelye, V., et al., *Reverse osmosis on open intake seawater: pre-treatment strategy*.* Desalination, 2004. **167**: p. 191-200.

44. Chua, K., M. Hawlader, and A. Malek, *Pretreatment of seawater: Results of pilot trials in Singapore.* Desalination, 2003. **159**(3): p. 225-243.

45. Glueckstern, P., M. Priel, and M. Wilf, *Field evaluation of capillary UF technology as a* pretreatment *for large seawater RO systems* 1.* Desalination, 2002. **147**(1-3): p. 55-62.

46. Burashid, K. and A.R. Hussain, *Seawater RO plant operation and maintenance experience: Addur desalination plant operation assessment.* Desalination, 2004. **165**(1-3): p. 11-22.

47. Sinha, S., *Precursors removal by Coagulation* in *Civil (Environmental) Engineering*2001, University of Colorado-Boulder: Boulder.

48. Snoeyink, V.L., *Occurrence and Removal of Volatile Organic Chemicals from Drinking* Water, in *AWWA Research Foundation/KIWA Report*1983, AWWA Research Foundation: Denver.

49. J.Weber, V.L.S.a.J.W., *Progress in Surface and Membrane Science*, in *J. F. Danielli, ed.*1972, Pergamon.

50. SHIMADZU. *TOC-V CPH* 2011; Available from: http://www.shimadzu.com/an/toc/lab/index.html.

51. SCIENTIFIC, T. *CyperScan pH6000*. 2011; Available from: http://www.eutechinst.com/pdt-type-cyberscan-premium-ph6000.html.

52. Instruments, OAKTON, 2011.

53. Company, H. *2100AN Laboratory Turbidimeter, EPA, 115 Vac*. 2011 22 July, 2011]; Available from: http://www.hach.com/2100an-laboratory-turbidimeter-epa-115-vac/product?id=7640450972.

54. Ltd, M.I. *Zetasizer Nano*. 2011; Available from: http://www.malvern.com/labeng/products/zetasizer/zetasizer_nano/zetasizer_nano_zs.htm.

55. Environmental Sciences Section, I.C.U., *ESS Method 340.2: Total Suspended Solids, Mass Balance (Dried at 103-105C)*, in *Procedure for Total Suspended Solids*1993: Wisconsin State Lab of Hygiene, 465 Henry Mall, Madison, WI 53706.